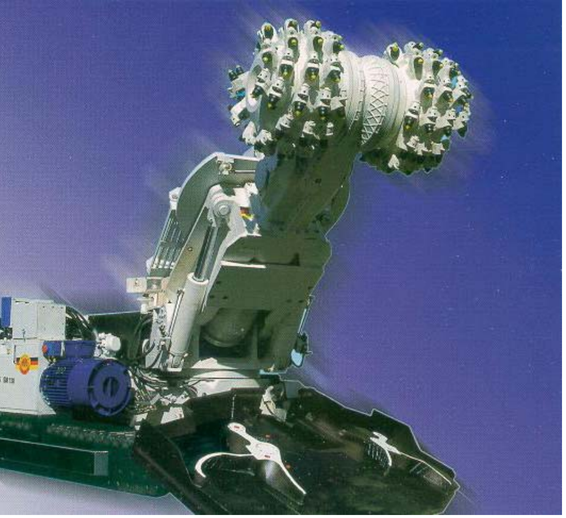
Novel Superhard Materials and Nanostructured Diamond Composites for Multiple Industrial Applications

Principal Investigator: **Yusheng Zhao**
(CPS# 1795)
LANSCE-12, MS-H805
Los Alamos National Laboratory
Los Alamos, NM 87545
(505)-667-3886, yzhao@lanl.gov

Academic Partners:
Texas Christian University
John Hopkins University
SUNY at Stony Brook

Industrial Partners:
U. S. Synthetics
Smith MegaDiamonds
Ringwood Superabrasives
Rock Bit International

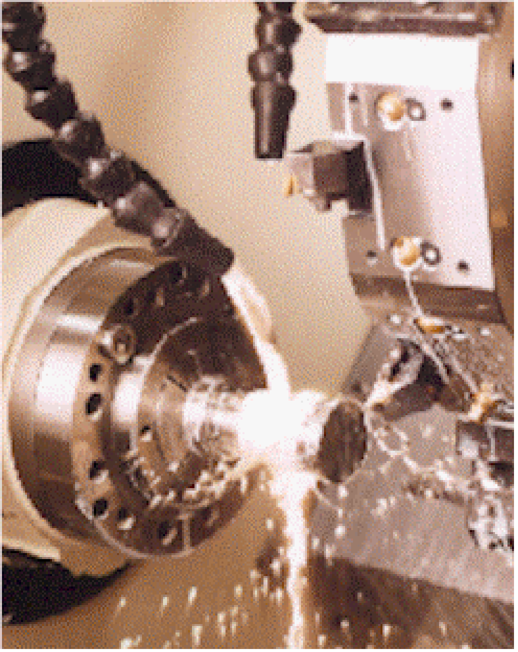
ITP 2004 Materials, Glass, and Sensors Project and Portfolio Review Meeting
June 21-24, 2004, Crystal Gateway Marriott, Arlington, VA

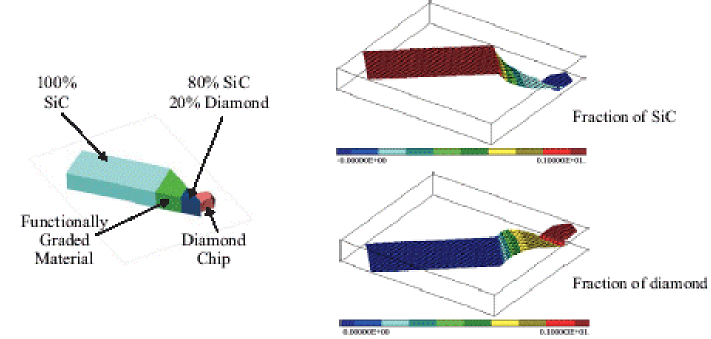


Applications
(Market)

Construction / Rock Cutting / Drilling & Mining ------- $1.6 Billion

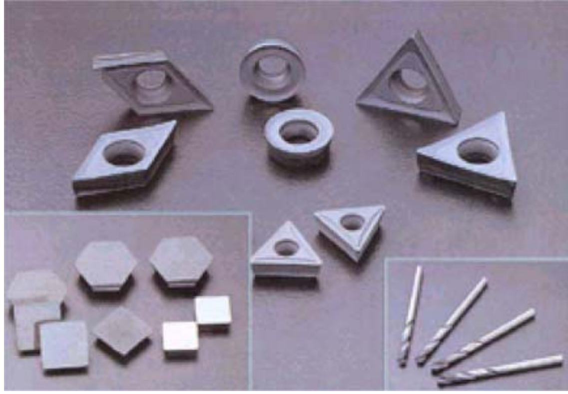
($1.0B) ($0.5B) ($0.1B) **($1.6B)**





(a) Diamond cutter tool consists of several distinct material regions

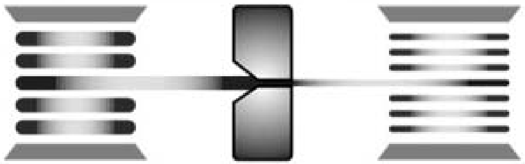
(b) Fractions of each material vary throughout the solid but always add to 1



($1.00B) ($0.05B) ($0.20B)

Machinery Tooling / Wire Drawing / Grinding / & Automobile Industrials -------- $1.40 Billion

($0.15B) **($1.40B)**



Superhard Tools Are Widely Used in Modern Industries

!! *Hardness, Toughness, Strength, & Thermal Stability* !!

Industrial Needs (Pain):

Blunting and shattering of the cutting edges and drilling bits greatly slow down the machining and penetrating processes.

— ***waste time & energy***

Conventional diamond compacts

- Metal bonding (Cobalt, Nickel, …)
- Low thermal stability (T_G< 900ºC)
- Low fracture toughness (< 8 MPa·$m^{1/2}$)

Nanostructured diamond composites

- Ceramic bonding (SiC, TiC, …)
- High thermal stability (T_G>1200ºC)
- High fracture toughness (>12 MPa·$m^{1/2}$)

Technological Solution (Pill):

Harder, tougher, last "forever" superhard & superabrasive materials to speed up the machining and drilling processes.

— ***increase efficiency***

Objective:

Harder and Tougher (*simultaneously*) Materials for Industrial Applications such as drilling, cutting, grinding, and machining, *etc*.

Approach:

High Energy Ball Milling Preparation for Amorphous/Nanostructures

High-Pressure and High-Temperature Synthesis (*Reactive Sintering*)

Nanotube Reinforcement of Composites

Mechanical (*Industrial*) Characterization

Field (*drilling*) and Machinery (*cutting*) Tests with Industrial Partner.

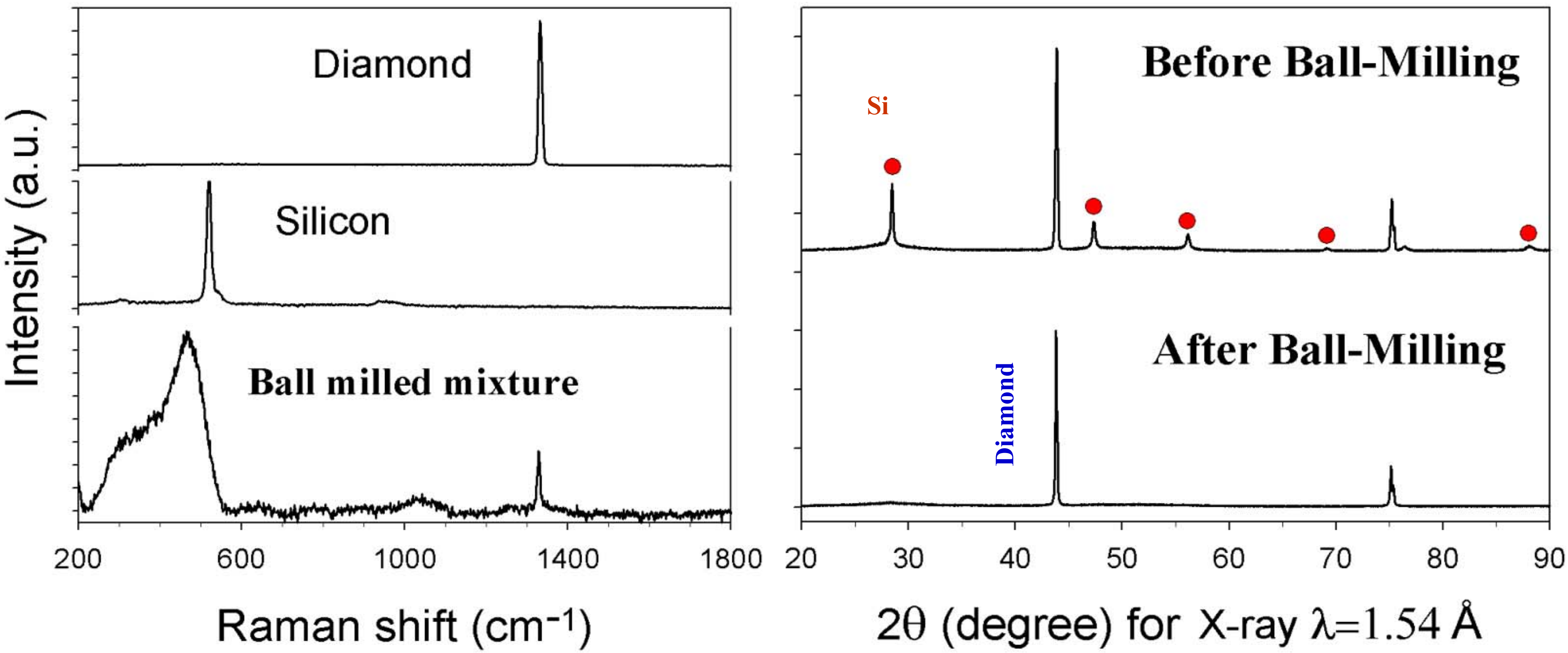
Commercialization:

Multi-Billion dollar markets in making of drill bits, machinery tools; Great potentials in savings of money, time, energy, & environments.

Diamond Composites with Nanocrystalline SiC Bonding

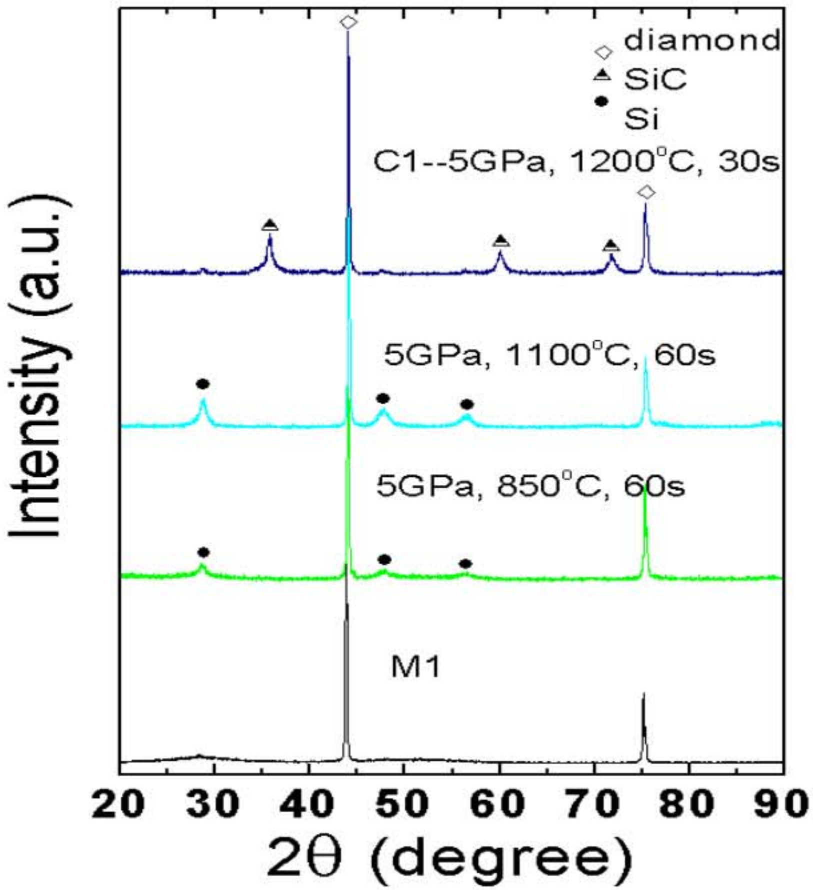
Starting material: M1: diamond(<10μm)/a-Si mixture *(Ball milling!)*
M2: diamond(~250nm)/Si(~10nm) mixture

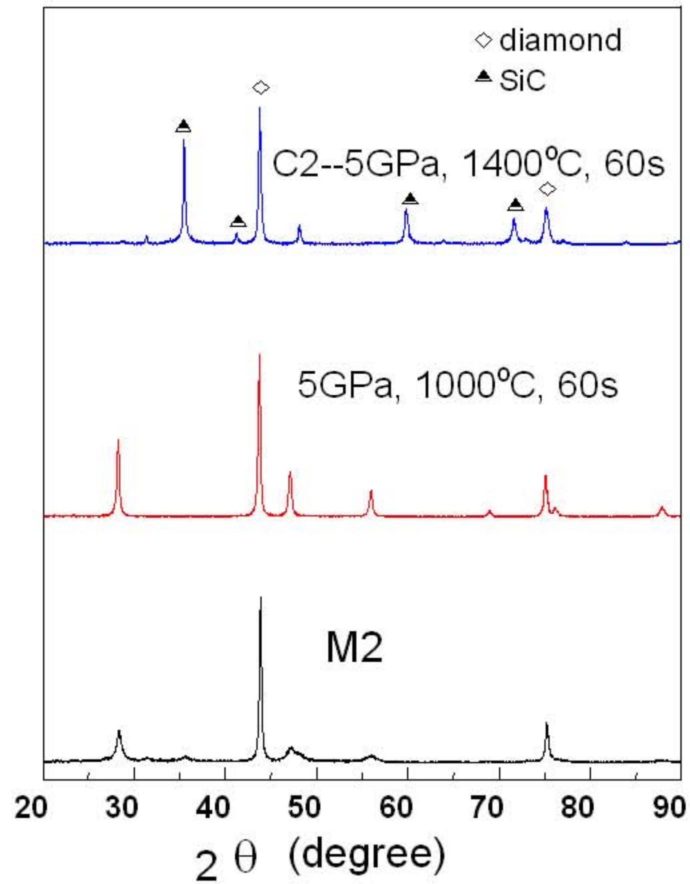
Diamond + Si Mixture



The SiC bonding matrix has much higher thermal stability range than the metal bonding, such as Co, Fe, & Ni, etc.

Thermally Stable Diamond-SiC Composites with Nanocrystalline Bonding Matrix





High *P-T* reactive sintering !!!

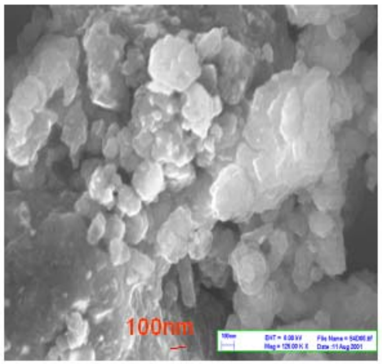
carbon (*diamond*) and amorphous silicon

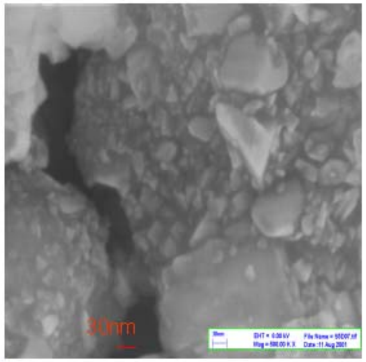
to form nanocrystalline silicon carbide (SiC) matrix

NanoSynthesis:

Amorphous precursors, massive and homogenous distribution of nuclei;

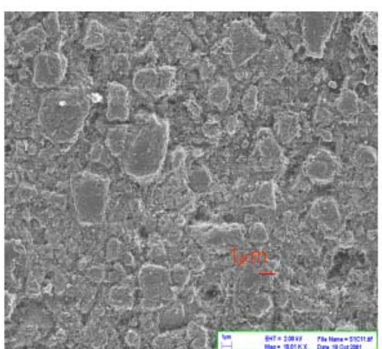
Interplay and tuning between pressure, temperature, and sintering time.

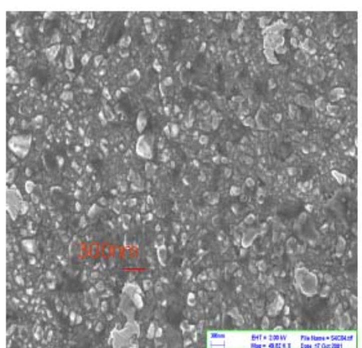




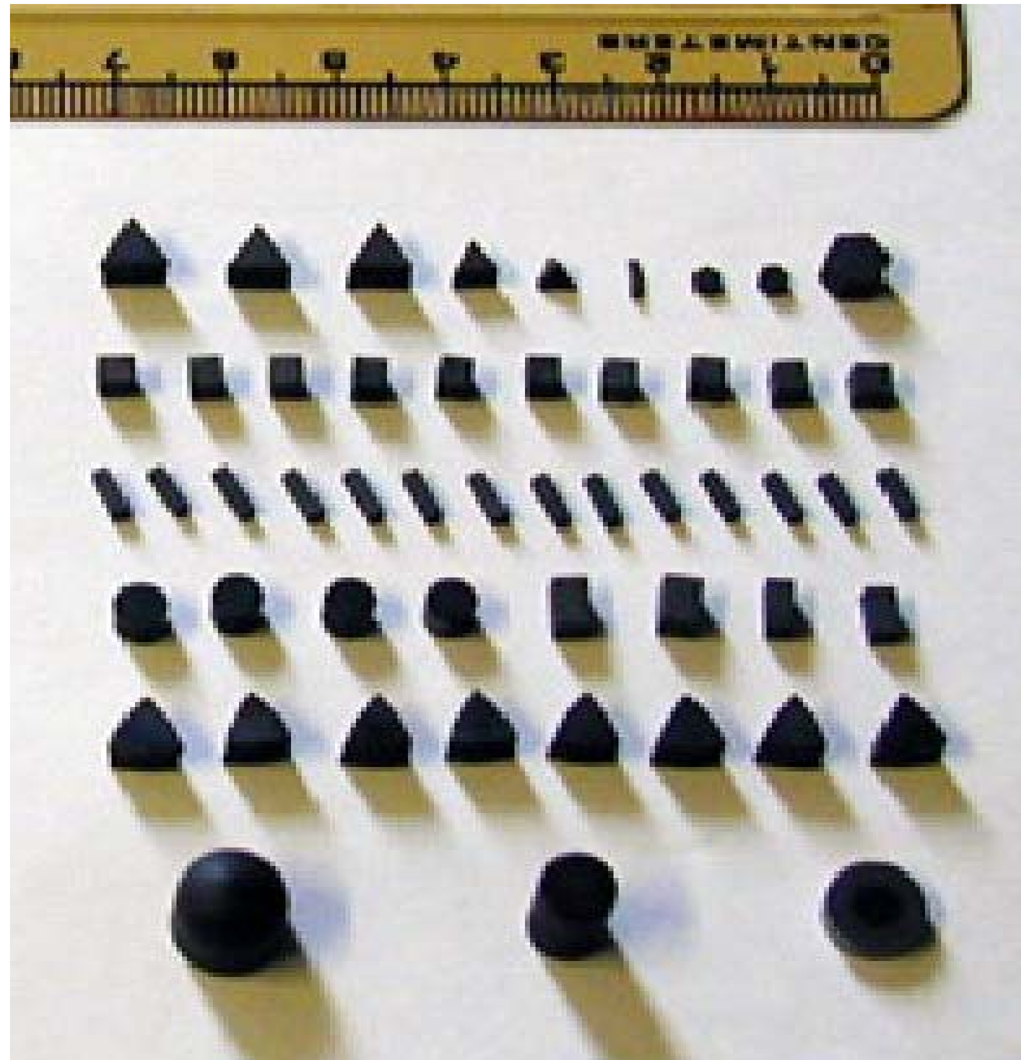
M1 Starting M2

b. SEM picture of M1, M2 and compsites sintered at 5.0GPa



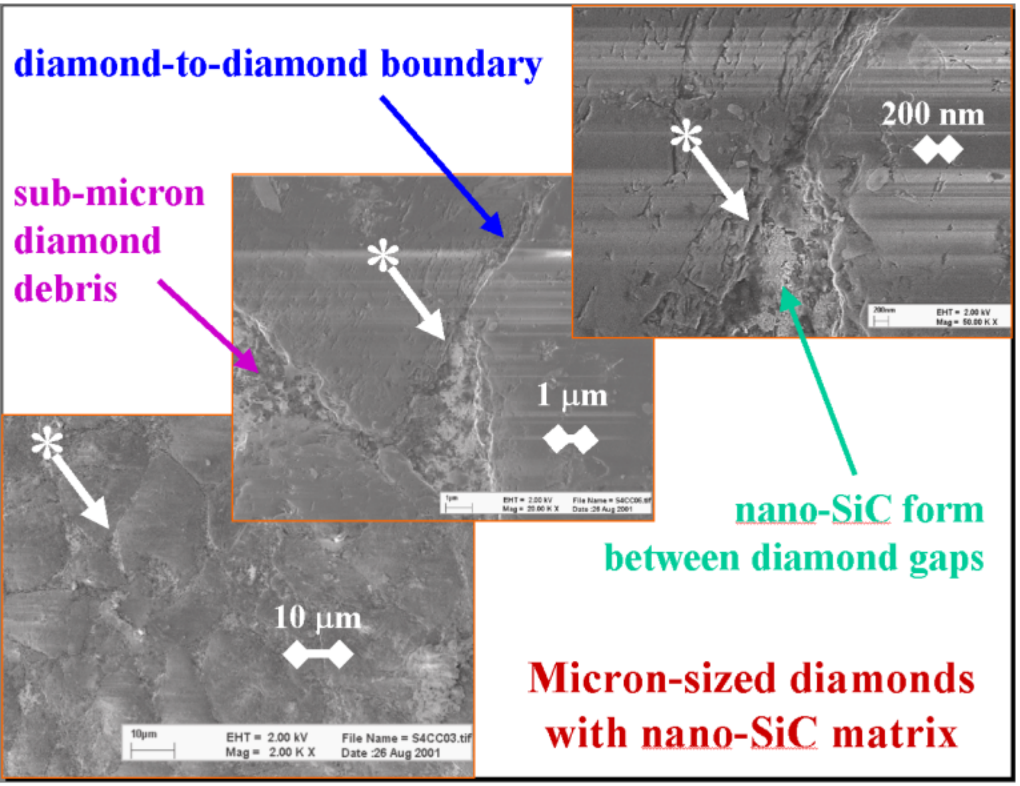


C1 High *P-T* C2



Interplay of *P-T-t* to control the formation of nano-matrix

Nucleation and crystallization of high density SiC phase from amorphous/molten Si in reaction with carbon is ***thermodynamically*** favored under **high-pressure**, as the amorphous Si and/or its molten phase has a lower density and a higher compressibility than the crystalline SiC phase.



Nano-Synthesis -----

Hybrid micron-/nano- diamonds and nano-SiC matrix

High *P-T* reactive sintering removes diamond defects

Reduction of un-reacted silicon and back-transformed graphite

Readily achievable pressure and temperature range

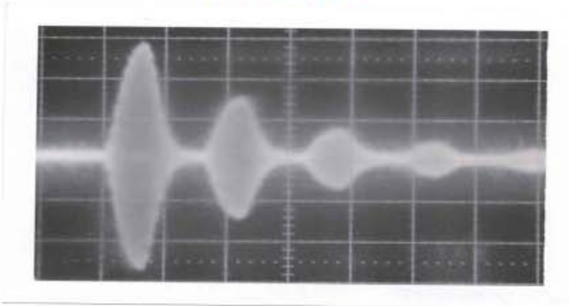
The grain growth of a large number of crystalline SiC nuclei accompanied by long-range atomic rearrangements is ***kinetically*** hindered at **high-pressures**.

This balancing act between *thermodynamics* and *kinetics* leads to the formation of a nano-crystalline SiC matrix.

Mechanical Properties of Diamond-SiC Composites

a. Ultrasonic interferometry Measurement of Acoustic Elasticity

P-wave



S-wave

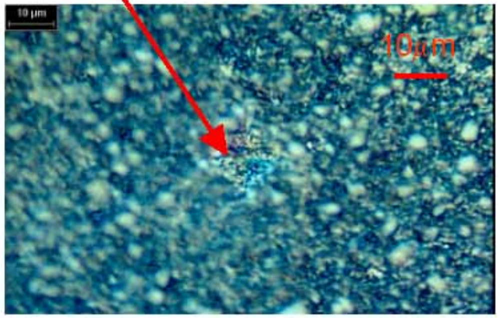
*Young's modulus:

Composites: 540GPa

SiC ceramic: 410GPa

b. Vickers hardness

Indentation
No crack visible
High fracture toughness



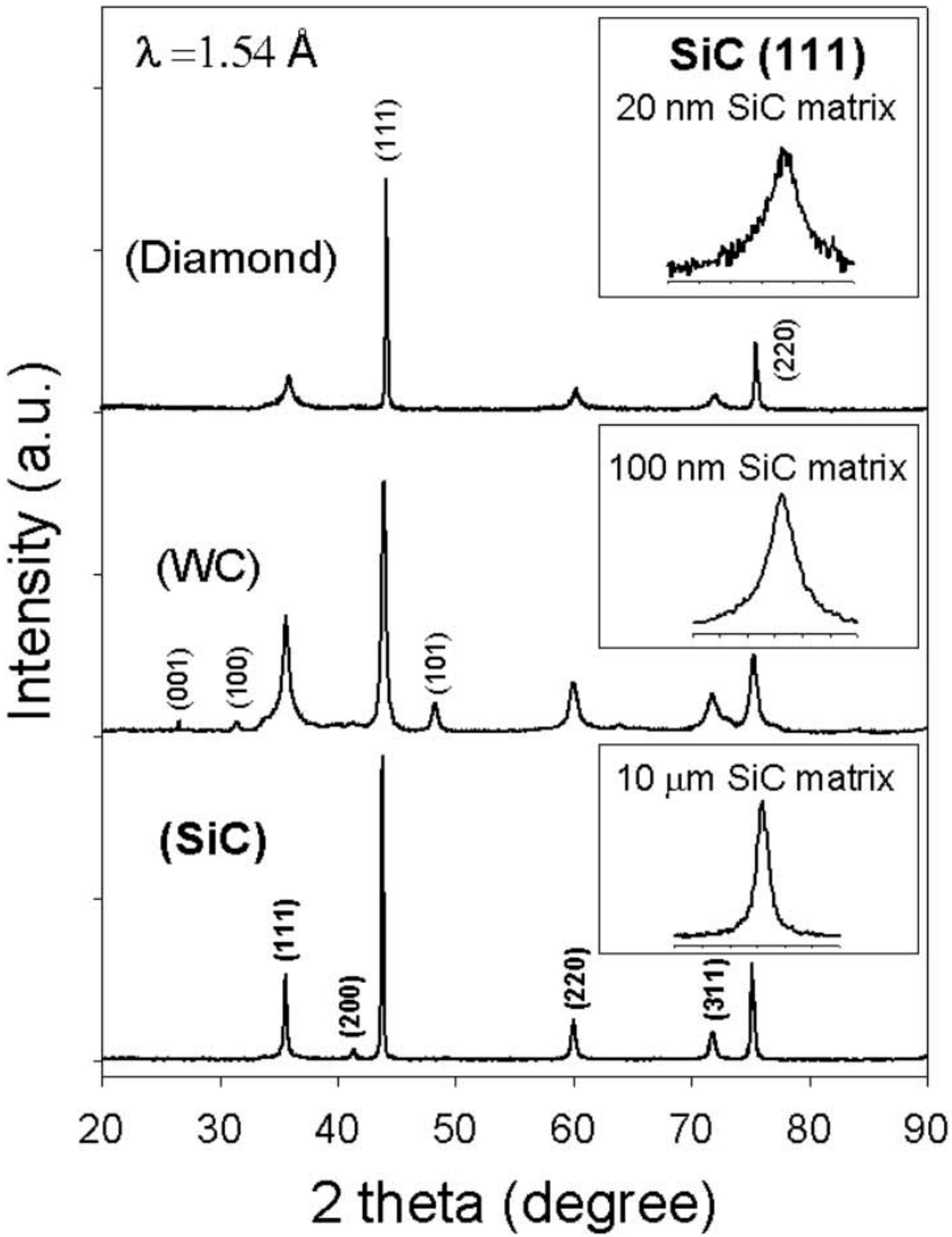
Composites sintered at 5.0 GPa

Sample No.	Starting material	T (°C)	Time (sec.)	Density (g/cm^3)	SiC (wt%)	Residual Si (wt%)	Vickers hardness (GPa)
S1	M1	1200	30	3.33	21.6	2.2	36±2
S2	M1	1400	30	3.35	21.3	0	45±5
S3	M2	1200	60	3.01	4.3	14.6	16±1
S4	M2	1400	20	3.17	12.8	8.1	25±2
S5	M2	1400	40	3.32	21.9	1.4	44±5
S6	M2	1400	60	3.32	21.4	1.7	44±5

*High H_V (~45GPa) at moderate P-T conditions (5GPa, 1400°C)

Diamond-SiC composites

synthesis condition: 5 GPa, 1800 K, 30 sec



We tested three sample preparation procedures for high *P-T* synthesis of diamond-SiC composites:

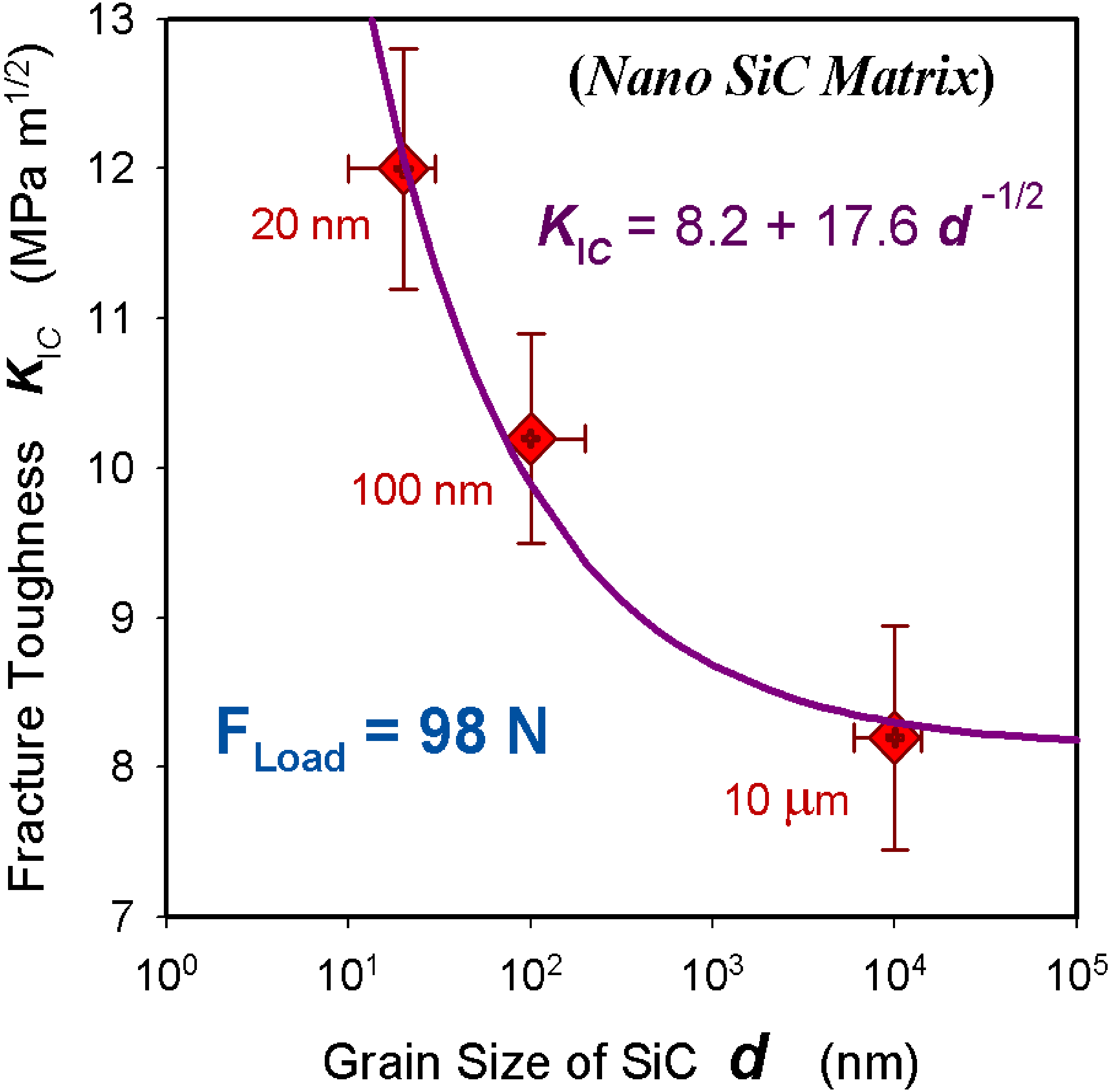
1) **a thorough mixture of diamond and amorphous silicon;**
2) **thorough wet mixing of nano-diamond & silicon in methanol;**
3) **Si-melt infiltration into diamond aggregates under high *P-T*.**

The resulting products have distinct SiC matrices of various grain sizes: 20nm, 100nm, and 10,000nm, respectively.

The diamond participation speeds up the Si amorphisation process significantly

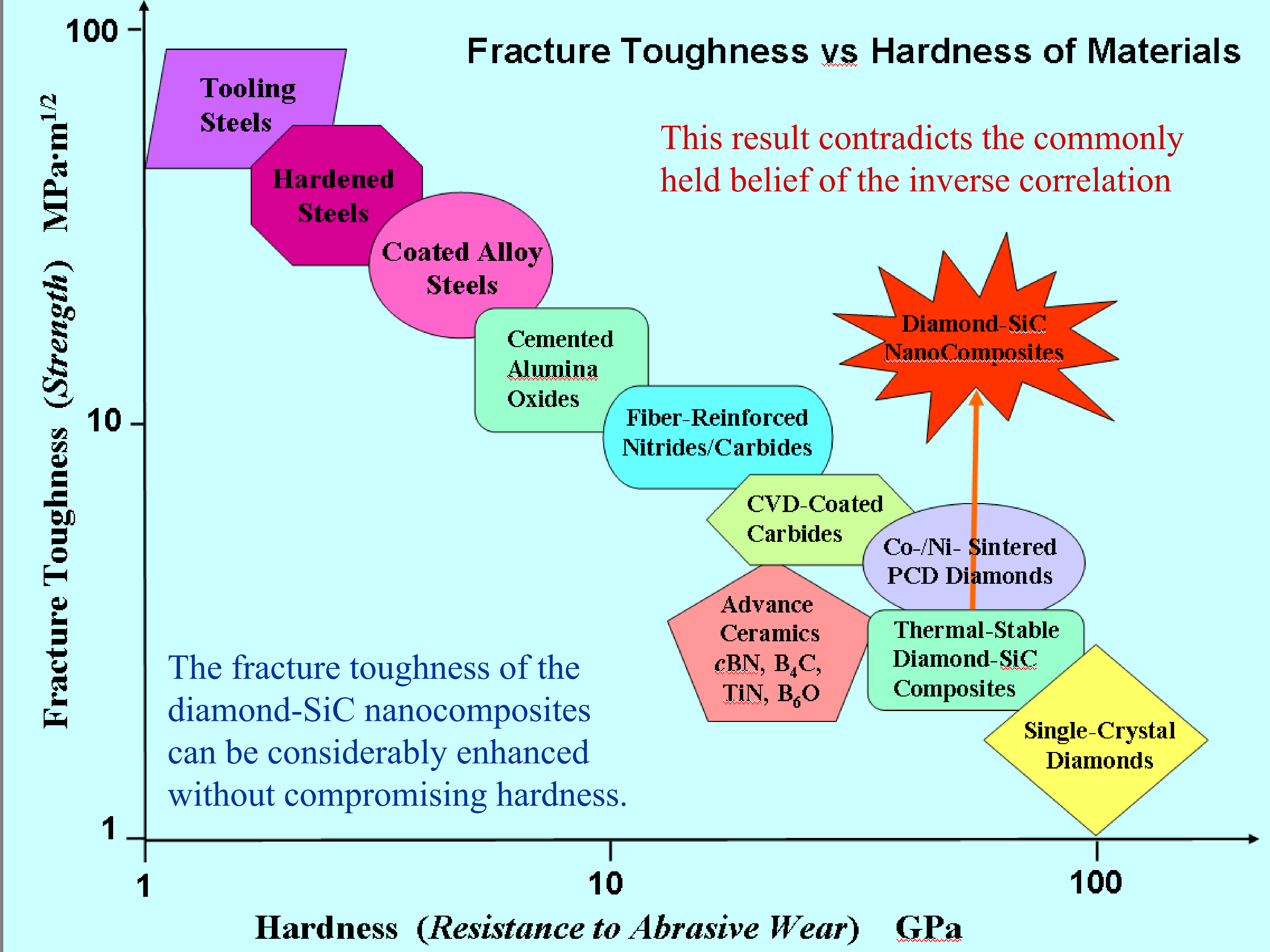
Overcome the "bottle-neck" problem of the infiltration method.

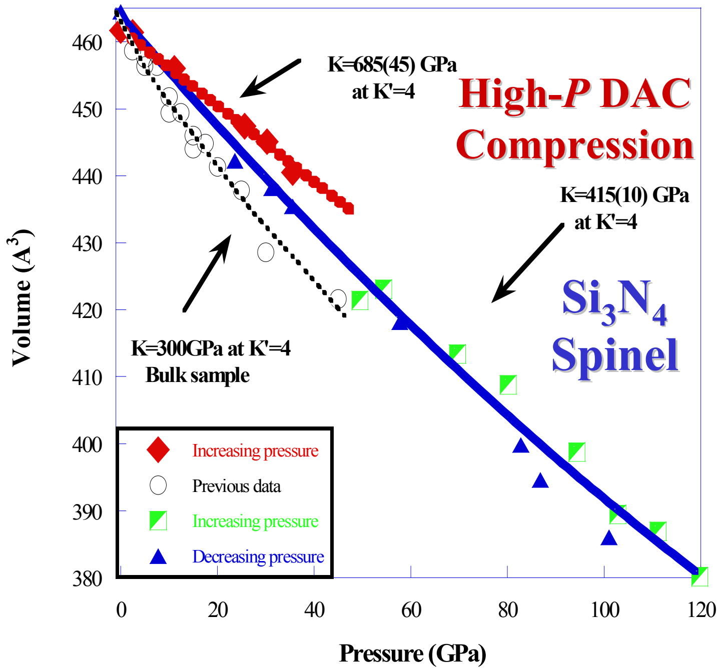
Nanostructured Diamond-SiC Composites



NanoSynthesis to NanoMechanics

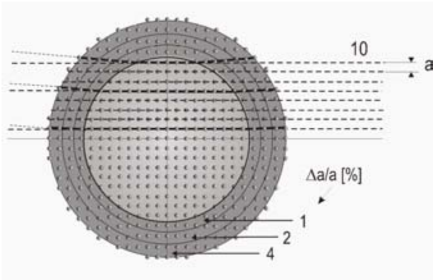
First experiment to demonstrate effect of nanomatrix for composite materials

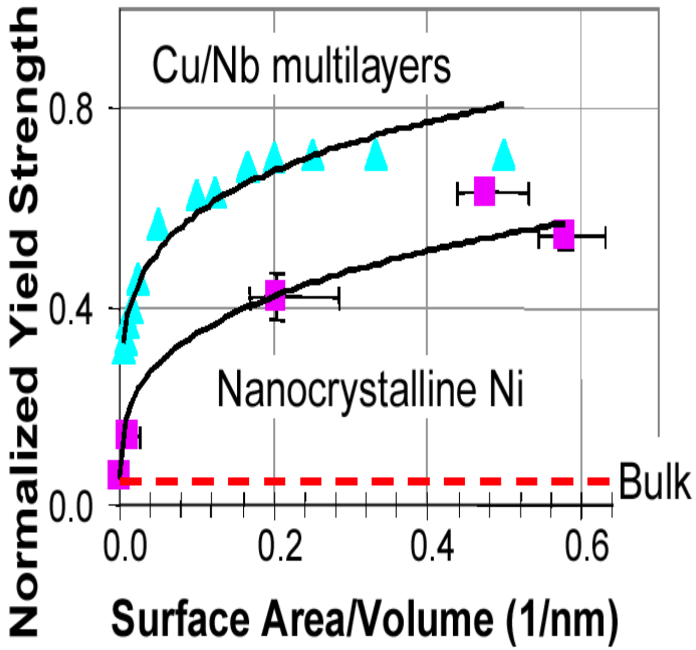

Fracture Toughness vs Hardness of Materials
This result contradicts the commonly held belief of the inverse correlation
100
10
1
Fracture Toughness (Strength) MPa·m$^{1/2}$
Tooling Steels
Hardened Steels
Coated Alloy Steels
Cemented Alumina Oxides
Fiber-Reinforced Nitrides/Carbides
CVD-Coated Carbides
Diamond-SiC NanoComposites
Co-/Ni- Sintered PCD Diamonds
Advance Ceramics cBN, B_4C, TiN, B_6O
Thermal-Stable Diamond-SiC Composites
Single-Crystal Diamonds
The fracture toughness of the diamond-SiC nanocomposites can be considerably enhanced without compromising hardness.
1
10
100
Hardness (Resistance to Abrasive Wear) GPa



Nano-Mechanics -----

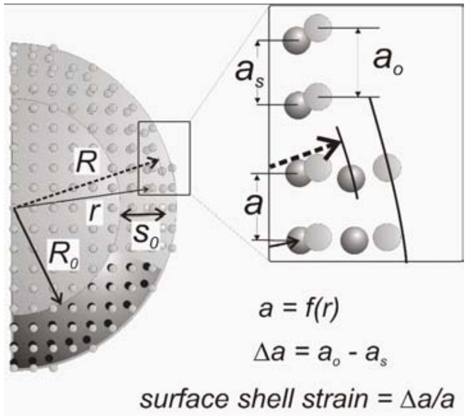
nanostructured materials with high surface-to-volume ratio show drastically increase of yield strength and fracture toughness as deformation mechanism changing from continuum (micro-scale) to discrete (nano-scale)



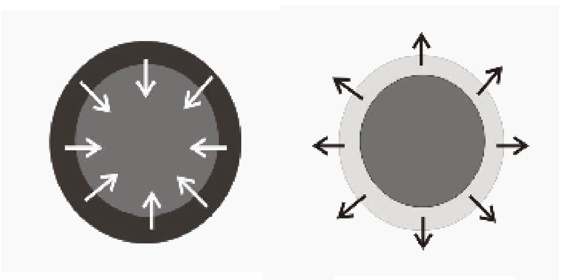


Bulk modulus of nano-particles increases greatly (> 40%)

Palosz et al. (2002)



Misra, Kung (LANL) Knapp, Follstaedt (SNL)



Compression ***Tension***

New mechanical behavior for high interface/volume ratio

Deformation and fracture of materials occur by multiplication/propagation of dislocations/vacancies/micro-cracks

Nanostructure eliminate those "bad agents"

Non-Disclosure Agreement
with Ringwood Superabrasive

Non-Disclosure Agreement
with U. S. Synthetics Corp.

Los Alamos
NATIONAL LABORATORY
Technology Transfer Division

To/MS: Distribution
From/MS: Patricia Grall, TT, MS C334
Phone/Fax: 5-3441/5-0154
E-mail: pgrall@lanl.gov
Symbol: NDA-04-4696
Date: March 1, 2004

Pat Grall

SUBJECT: **Non-Disclosure Agreement (NDA) NDA-04-4696: Notification of Execution Between The Regents of the University of California and Ringwood Superabrasives Pty Ltd**

The Technology Transfer (TT) Division has executed an NDA on behalf of **LANSCE-12.** The subject matter for this NDA is: **the University's technology in nano-structured diamond composites, Information embodied in DOE Case #S100,575 entitled 'Dia[illegible] Silicon Carbide Composite and Method for Prep[illegible]' data related to Ringwood's Intellectual [illegible]roperty and mark[illegible] of th[illegible] Univ[illegible] 02-3856 entitled 'Diamond-SIC Nanocomposites Sintered f[illegible]m a Mixture of Diamond and Silicon Nanopowders'** for the purpose **of conducting discussions to evaluate whether to enter into a contractual relationship.**

From scientific research to technological development

IN WITNESS WHEREOF, the parties have caused this Agreement (NDA-04-4696) to be executed by their duly authorized representatives.

Ringwood Superabrasives Pty Ltd

by
Len Kosharek
CEO

Date 27/FEB/2004

The Regents of the University of California
Los Alamos National Laboratory

by Patricia Grall
Patricia Grall
Technology Transfer Specialist, IBD

Date February 26, 2004

Los Alamos
NATIONAL LABORATORY
Industrial Business Development Division

To/MS: Distribution
From/MS: Patricia Grall, IBD, MS C334
Phone/Fax: 5-3441/5-0154
E-mail: pgrall@lanl.gov
Symbol: NDA-04-4609
Date: November 5, 2003

Pat Grall

SUBJECT: **Non-Disclosure Agreement (NDA) NDA-04-4609: Notification of Execution Between The Regents of the University of California and US Synthetic Corporation**

The Industrial Business Development Office (IBDO) has executed an NDA on behalf of **LANSCE-12.** The subject matter for this ND[illegible] is: **the Univers[illegible]y's technolog[illegible] in nano-str[illegible]ctured diamond compos[illegible]tes, Information embodied in D[illegible]E Case [illegible] characterization [illegible] related to US Synthetic's manufacturing process and [illegible]aterial characterization techniques of polycrystalline diamond compacts (PDC)** for the purpose of **conducting discussions to evaluate whether to enter into a contractual relationship.**

IV. IN WITNESS WHEREOF, the Parties have caused this Agreement (NDA-04-4609) to be executed in by their duly authorized representatives.

US Synthetic Corporation

by:
Name: Ken E. Bertagnolli
Title: ~~Research Director~~

Date: NOVEMBER 5, 2003

The Regents of the University of California
Los Alamos National Laboratory

by: Patricia Grall
Name: Patricia Grall
Title: Technology Transfer Specialist

Date: November 4, 2003

We are working hard to push the **R**esearch & **D**evelopment results into the industrial applications. We are arranging the test production of the nanostructured diamond composites with our starting materials using industrial setups, and also are going to conduct mechanical tests with industrial standards.

LANL-Smith ***Materials Transferring Agreement*** and ***Mechanical Test Agreement*** are also prepared / signed

Los Alamos
NATIONAL LABORATORY
Technology Transfer Division

To/MS: Distribution
From/MS: Patricia Grall, TT, MS C333
Phone/Fax: 5-3441/5-3125
E-mail: pgrall@lanl.gov Pat Grall
Symbol: NDA-04-4765
Date: May 10, 2004

SUBJECT: **Non-Disclosure Agreement (NDA) NDA-04-4765: Notification of Execution Between The Regents of the University of California and Smith International**

The Technology Transfer (TT) Division has executed an NDA on behalf of **LANSCE-12**. The subject matter for this NDA is: **the University's technology in nano-structured diamond composites, Information embodied in DOE Case#S100,575 entitled 'Diamond Silicon Carbide Composite and Method for Preparation', and data related to the characterization of the University's nano-structured diamond composite materials, and Information relating to specific Megadiamond high-temperature/high-pressure processing of nanodiamond composite and potential applications of this material** for the purpose **of conducting discussions to evaluate whether to enter into a contractual relationship.**

As employees of the University, we are bound to the terms of the NDA by your employment agreement. In instances where the industrial partner is supplying the University with information, this information should be protected with the same care as the University protects its own information.

From laboratory experiment to industrial manufacture

One can never place enough emphasis on maintaining the confidentiality of information. Disclosure of this information would leave the University open for suit and would severely impair the ability of the University to gain other industrial partners for collaborative activities.

It is important that you read the attached NDA and understand the terms and conditions in it. Of particular importance are the following terms:

- **disclosure period of the agreement is: one (1) year Ending: 4/30/2005**
- **all proprietary information disclosed by one party to the other party must be in written or other permanent form and identified as proprietary by the originating party by clear and conspicuous markings.**
- **all non-written information must be put in writing within: fourteen (14) days**
- **each party must maintain the information it receives as proprietary for: three (3) years from the date of disclosure.**

If you have any questions on the Laboratory's policy on employees' responsibilities concerning identification and protection of information, refer to Administration Manual 721. This policy can be viewed at the following address: **http://iosun.lanl.gov:2001/htmls/policy/adm/am700.html**. You can also view the FSS publications concerning the same at: **http://www.lanl.gov/Internal/divisions/fss/fss-16/htmls/release.html**

As always, please feel free to call me if you have any questions.

Distribution:
Yusheng Zhao, LANSCE-12, MS H805, w/enc.
Alan J. Hurd, LANSCE-12, MS H805, w/enc.
Jiang Qian, LANSCE-12, MS H805, w/enc.
Christine T. Ramos, TT, MS C333, w/enc.
Paul W. Lisowski, LANSCE-DO, MS H845, w/enc.
Charles E. Gibson, TT, MS C333, w/enc.
Patricia B. Duran, TT, MS C334, w/enc.
NDA File

11. This Agreement contains the entire understanding between the Parties, superseding all prior or contemporaneous communications, agreements, and understandings between the Parties with respect to the disclosure and protection of Information. This Agreement shall not be amended except by further written agreement executed by the duly authorized representatives of the Parties.

12. The Recipient and their employees, contractors, agents, consultants and employees thereof shall not use or disclose any Information or any other Information disclosed hereunder in any manner contrary to the laws and regulations of the United States of America, or any agency thereof, including but not limited to the Export Administration Regulations of the U.S. Department of Commerce.

13. This Agreement shall not constitute any representation, warranty or guarantee to the Recipient by the Discloser with respect to non-infringement of patents or other rights of any other party.

14. The Discloser shall not be liable to the Recipient for any errors or omissions in the Information disclosed by it under this Agreement nor for the use or the results of the use of the Information by the Recipient.

15. Each party represents that it is not now a party to, and shall not enter into any agreement in conflict with this Agreement.

16. Where a court of competent jurisdiction declares any provision of this Agreement to be invalid or unenforceable, the remaining provisions shall continue in full force and effect and all rights accrued under the enforceable provisions shall survive such declaration.

17. This Agreement shall be effective as of the date of the latest signature below.

18. This Agreement may be signed in one or more counterparts (including faxed copies), each of which shall be deemed one and the same original.

IV. IN WITNESS WHEREOF, the Parties have caused this Agreement **(NDA-04-4765)** to be executed in by their duly authorized representatives.

Smith International

by: Dan Belnap
Name: Dan Belnap
Title: R&D Manager
Date: 4/30/04

The Regents of the University of California
Los Alamos National Laboratory

by: Patricia Grall
Name: Patricia Grall
Title: Technology Transfer Specialist
Date: April 12, 2004

Non-Disclosure Agreement with Smith MegaDiamonds

PCD Enhanced Insert Impact on WC-Co Anvils

Dan Belnap, Ph.D.
R&D Manager, Smith Megadiamond

***Diamond and Related Materials**, (unpublished)*

The carbide was observed to transition from localized plastic deformation at lower impact loads to severe cracking and deformation at high impact loads.

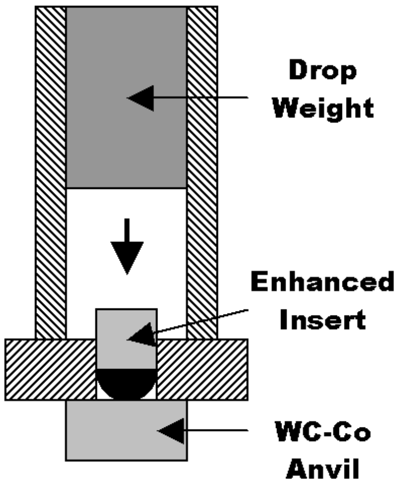


Figure 1. Impact testing schematic.

LANL and Smith MegaDiamond and U.S. Synthetic have signed agreements to transfer starting materials for industrial synthesis and to further conduct mechanical test using industrial standards.

Impacting, Drilling, Cutting Tests on Granites & Limestone

In contrast to the WC-Co anvils, the enhanced polycrystalline diamond insert damage was relatively minor, observed during impact testing.

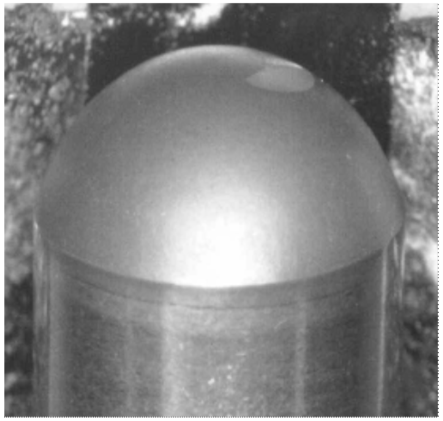
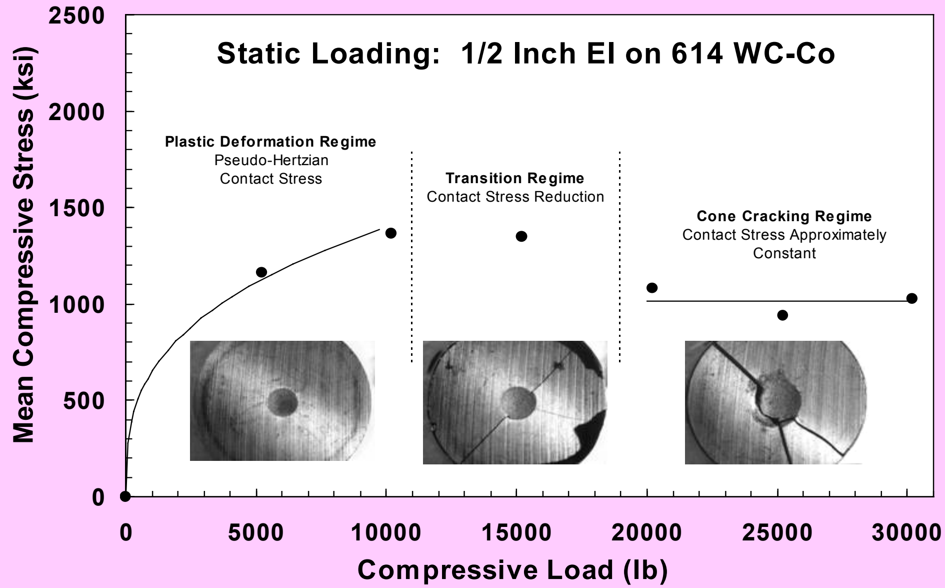


Figure 3. Enhanced insert with impact damage.



LANL-TCU-ISM-RBI

Joint Efforts

The mounting of WC-Diamond inserts onto the tri-conical drill bit of RBI

Study kinetics of reaction between diamond composite core and titanium and determine optimal brazing temperature.

Study possibilities of brazing WC inserts with diamond composites cores in different inert atmospheres.

Design several types of the WC–diamond composite inserts for application in cone bits: *Conical-type* and *Chisel-type*.

Real case: ***Oil field drilling!***

Case Study – Oil Drilling

to drill a 7000 feet depth well in East Texas (*average well 5500 feet*)

- **Conventional bit**

  Soft rock formation:
  PCD bit, 100 ft/h

  Hard rock formation:
  WC bit, 20 ft/h

  Down-time to change bit
  24 ~ 48 hour

  Danger of abandon the well

- **Novel nano-composites diamond bit**

  Soft & hard rock formation
  One bit, 150 & 100 ft/h
  Less bit changing

  - 7 bits reduced to 4 bits
  - 6 trips reduced to 3 trips
  - time/energy/money saving
    2 ~ 4 times

- Total well drilling in U.S. is 150~180 million feet per year
- It costs $40~50 Billion annually for average $300 per feet
- Total cost for petroleum industry is about $10 Billion/year

Cost saving (*annual*) with adopting novel nano-composite bits can be as much as $300 ~ $500 million per year (*U.S. drilling industry alone*!)

Tuesday, December 16, 2003

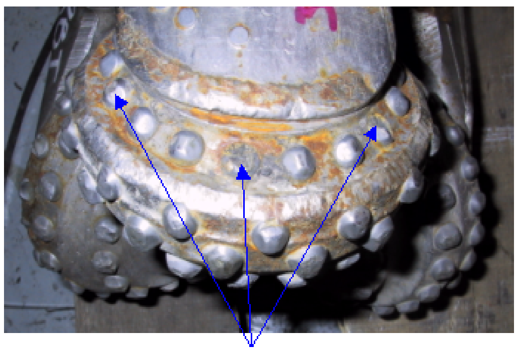
Canadian Drill Site
Oil Well Drilling

A quick examination of the returned Canadian bit which had 18 of the special composite/tungsten carbide inserts revealed the following

Number of Composite Inserts	Number of Tungsten Carbide Inserts	Number of failed Composite Inserts	Number of failed Tungsten Carbide Inserts
18	36	5.5	1

One can see that the percentage of failed composite inserts is much higher (5.5/18 = 31%) as opposed to the number of failed Tungsten Carbide inserts (1/36=3%). The rows on the rockbit where both of these inserts were placed is a row which is not considered to be a main cutting row. They were placed in the reaming gage row, which should experience much lower load forces as opposed to the main cutting rows of a rockbit.

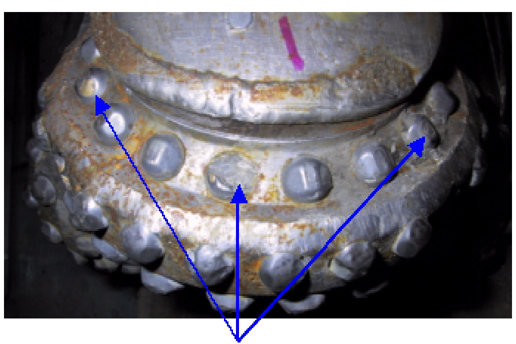
The two photos below show two of the rollercones that had the composite inserts in them



Composite inserts, the two on the right have fractured and failed. The Tungsten Carbide inserts between them are unaffected.

RockBit International

Composite inserts on the ends are intact while the insert in the middle has fractured.



USSynthetic Technical Report

TITLE: Evaluation of LANL Nano-Structured Diamond Composite Material		
AUTHOR: Ken Bertagnolli	DATE: January 22, 2004	REPORT NO.: KEB-01-2004

SUMMARY

The purpose of this investigation was to evaluate the performance of five nano-structured diamond composite samples supplied by Los Alamos National Laboratory and determine their suitability for the oil and gas drilling market. The following conclusions can be made from this investigation:

- The wear resistance of the LANL samples was 100 times less than a standard US Synthetic PDC product, much too low for drilling applications.
- The LANL samples had insufficient strength for drilling applications. One sample cracked in half, one sample had a major crack through the center, and another sample generated cracks in the wearflat during the granite-log abrasion test.
- Two of the five samples lacked sufficient edge quality to conduct meaningful tests.

Overall, the LANL samples lack sufficient strength and wear resistance to be applicable to the oil and gas drilling market. Future development to improve these properties could make this material more suitable to the harsh downhole drilling conditions.

Improvements are desperately needed!

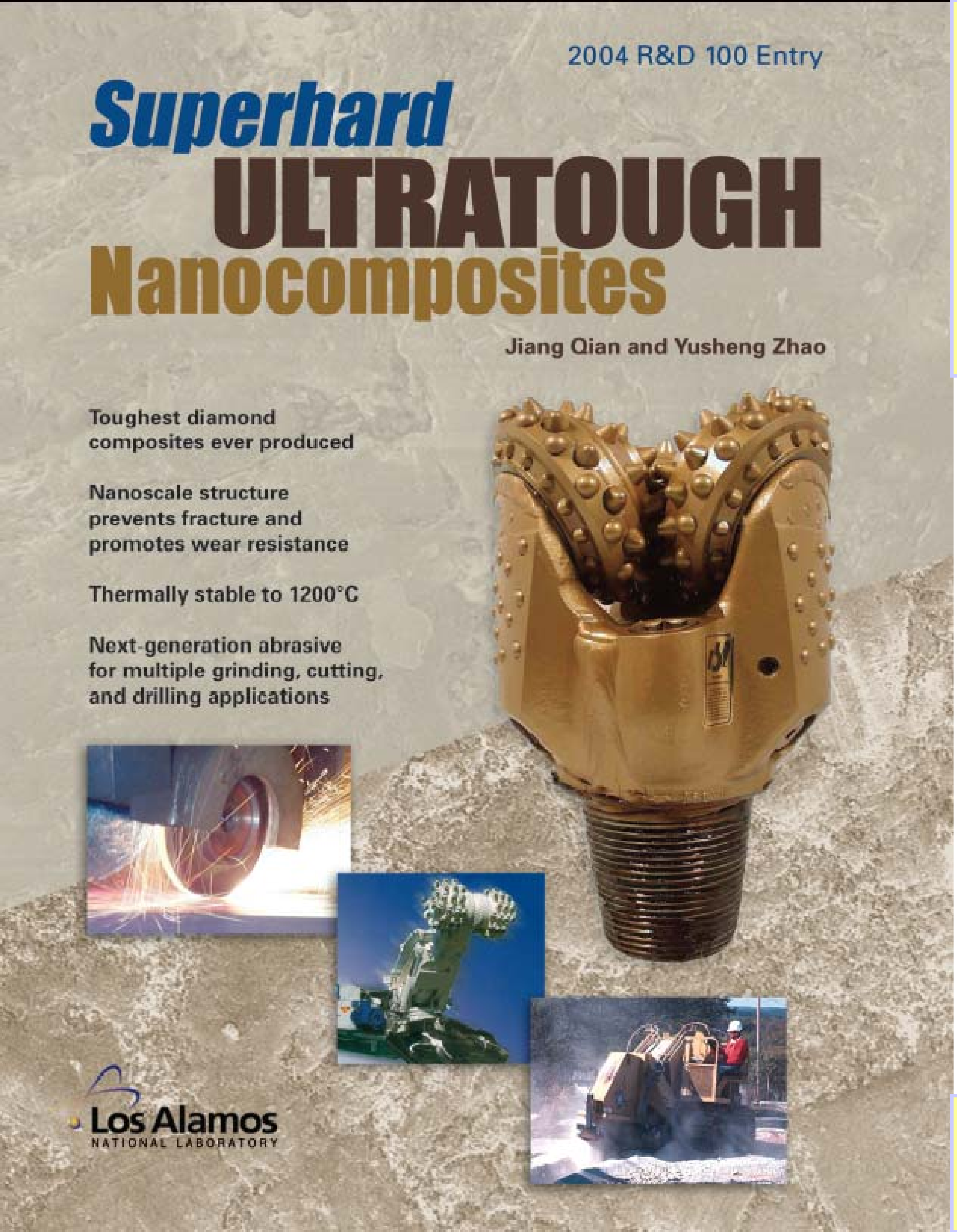
INTRODUCTION

Five nano-structured diamond composite samples were given to US Synthetic by Dr. Yusheng Zhao of Los Alamos National Laboratory on November 17, 2003. The composition of each sample is summarized in Table 1.

Table 1. LANL sample composition.

	Description	Observations
1	5-10 micron diamond (70 wt%) + 100nm diamond (10 wt%) + silicon (20 wt%)	Ground edge with some wearflats, possibly a previous wear test
2	5-10 micron diamond (70 wt%) + 100nm diamond (10 wt%) + silicon (20 wt%)	Unground, rough edge, not suitable for testing.
3	5-10 micron diamond (70 wt%) + 100nm diamond (10 wt%) + silicon (20 wt%)	Ground edge with five hardness indenter marks and cracks.
4	250 nm diamond (75 wt%) + 5nm diamond (5 wt%) + silicon (20 wt%)	Ground edge.
5	250 nm diamond (75 wt%) + 5nm diamond (5 wt%) + silicon (20 wt%)	Ground edge with many edge chips and a large crater on one side, not suitable for testing.

© 2004 US Synthetic Corporation
The material contained in this document is proprietary to US Synthetic Corporation and may not be reproduced, published, or distributed in any form or disclosed in whole or in part without the authorization of US Synthetic Corp.



Nanostructured Diamond-SiC Composite Materialss

with Superhardness & Ultratoughness

are highly appraised in many industrial applications

— U. S. Patents *(one allowed)* —

— R&D 100 Award *(2004 entry)* —

*Endorsement letters for LANL entry of **R&D 100** Award "Superhard & Ultratough NanoComposites" from diamonds and drill-bit industrial manufactures*

Ringwood Superabrasives

Ringwood Superabrasives Pty Limited
ACN 100 072 848

111-113 Gladstone Street
PO Box 1929
Fyshwick ACT 2609
Australia

Telephone +61 2 6283 0800
Facsimile +61 2 6239 3266
Web www.ringwoodsuperabrasives.com

31 March , 2004

R & D 100 Awards
2000 Clearwater Drive
Oak Brook, IL 60523

Dear Selection Committee:

We are one of the leading global manufacturers of high performance, polycrystalline diamond and silicon carbide composite materials. We hold 5 worldwide patents on the manufacture of this type of material. It is rare of us to see a new and creative approach to the manufacture of diamond composites. We believe that Jiang Qian and Yusheng Zhao of Los Alamos National Laboratory (LANL) have developed a material with highly desirable properties in our industry. Our Head of R&D, Dr. Charles Montross, an internationally known ceramic expert, sees novel IP within the details disclosed to us and we intend to work with LANL to develop the full market potential for this material. The most exciting feature is the fracture toughness of this material. It is very high and should open new multi-million dollar markets for us. These markets have been asking for these properties for many years. The LANL "Superhard, Ultratough Nanocomposites" are a quantum step towards satisfying that market demand. In biomedical applications, such as orthopaedics, it has the potential to improve the quality of life for countless people worldwide. I encourage your consideration for the Los Alamos project and their product of "Superhard, Ultratough Nanocomposites" for an R&D 100 Award.

As Chief Executive Officer of Ringwood Superabrasives, manufacturers of ultrahard materials (cBN and PCD), I look forward to becoming an industrial partner of the LANL project, which is supported by the DOE-EERE_IMF and DoD/DOE_MOU programs. I commend the LANL team for its focus on the commercial aspects of this significant material development. Bridging the gap between research and industry is a long sought after goal that was well achieved by Yusheng and Jiang. The focus of Nanocomposites has long been a point of interest to us and by being an industrial partner with the LANL project, it will speed our progress in this area.

Sincerely,

Len Kosharek
Chief Executive Officer

DiaCom Cutting Edge Solutions for Industry CubiCom

GEARHART
ROCKBIT INTERNATIONAL L.P.

February 5, 2004

R & D 100 Awards
2000 Clearwater Drive
Oak Brook, IL 60523

Dear Selection Committee:

I am pleased to endorse *Superhard Ultratough Nanocomposites* for an R&D 100 Award. Based on our laboratory and real-world field tests, these nanostructured diamond/silicon carbide composites appear to be an important new material of significant—possibly revolutionary—economic benefit to the drilling industry.

As President and Chief Executive Officer of RBI-Gearhart, a manufacturer of drilling bits, I am familiar with the needs of the drilling industry.

My area of expertise is the technical development of improved oil and gas drilling tools and equipment for hostile environments. Such equipment is necessary to recover oil and gas reserves from the deeper and hotter depths both on land and offshore. I directly manage development teams for such work and have been recognized for my contributions to the industry with numerous honors from the Society of Petroleum Engineers, the Society of Professional Well Log Analysts and the American Society of Mechanical Engineers. I also hold various patents in this field.

RBI-Gearhart is studying methods for improving the performance of drill bits by using inserts tipped with the *Superhard Ultratough Nanocomposites* developed at LANL by Jiang Qian and Yusheng Zhao. We are the industrial partner of the LANL project, which is supported by the DoE-EE_IMF and DoD/DoE_MOU programs.

Superhard Ultratough Nanocomposites address a major challenge in the drilling industry: quick, effective drilling through hard rock formations as well as interbedded soft and hard formations that are often found geologically. Currently available tungsten carbide or polycrystalline diamond compact inserts often do not survive the huge dynamic impact and high temperature conditions that occur during the drilling process.

We used *Superhard Ultratough Nanocomposite* materials to fabricate inserts for a drilling bit and subjected the bit to both laboratory and field tests. We have completed three successful tests with these inserts.

In our tests, drilling bits with *Superhard Ultratough Nanocomposite* inserts averaged speeds of 100 feet/hour through hard rock formations and up to 150 ft/hour through soft rock. This is approximately 2 to 5 times faster than with conventional tungsten carbide and polycrystalline diamond compact inserts under similar conditions. These nanostructured diamond/silicon carbide composites last longer than conventional materials and do not need to be changed when interbedded hard and soft rock formations are encountered. This saves considerable time and expense because of the rig time required to change out a bit. We conservatively estimate that these novel cutters reduce drilling time by more than half on a typical 7,000 deep well in eastern Texas.

Superhard Ultratough Nanocomposites exhibit performance critical properties including superhardness and ultrahigh toughness enabling them to withstand the harsh conditions of the down-hole drilling environment. They are cost effective and with continued improvement have the potential to create a large economic impact on the drilling industry. These new materials, as they become commercially available, could save more than $200 million a year for the US drilling industry alone and would have broad applications in other industries as well.

Sincerely,

Marvin Gearhart
President

APIQR REGISTERED FIRM ISO 9001

1. Zhao Y., J. Qian, L.L. Daemen, C. Pantea, J. Zhang, G.A. Voronin and T.W. Zerda, Enhancement of fracture toughness in nanostructured diamondSiC composites. Applied Physics Letters, Vol. 84, No. 8, 1356-1358 (2004)

2. Zhao Y., D. W. He, L. L. Daemen, T. Shen, R. B. Schwarz, Y. Zhu, D. L. Bish, J. Huang, J. Zhang, G. Shen, J. Qian, T. W. Zerda, Nanostructured Superhard BC_2N Material Bulks Synthesized under High P-T Conditions. Journal of Material Research, Vol. 17, No.12, 3139-3145, (2002).

3. Yan C., H.K. Mao, W. Li, J. Qian, Y. Zhao, R.J. Hemley, Ultrahard diamond single crystals from chemical vapor deposition. Phys. Stat. Sol. (a) 201, R25-R27, (2004). 2. He D., Y. Zhao, T. Sheng, R. B. Schwarz, J. Qian, K. A. Lokshin, S. Bobev, L. L. Daemen, H. K. Mao, J. Z. Hu, J. Shu, & J. Xu, Bulk Metallic Glass Gasket for High Prssure in situ X-ray Diffraction. Review of Scientific Instruments, Vol. 74, No.6, 3012-3016, (2003).

4. He D., Y. Zhao, L. Daemen, J. Qian, and T. Shen, Boron suboxide: As hard as cubic boron nitride. Appl. Phys. Lett., Vol. 81, No. 4 , 643-645, (2002).

5. Pantea C., J. Gubicza, T. Ungar, G.A. Voronin, T.W. Zerda, Dislocation density and graphitization of diamond crystals. Phys. Rev. B, vol. 66, no. 9, pp. 094106, (2002).

6. Pantea C., J. Qian, G. A. Voronin, T. W. Zerda, High pressure study of graphitization of diamond crystals. J. Appl. Phys., vol. 91, no.4, pp. 1957, (2002).

7. Qian J., C. Pantea, J. Huang, T. W. Zerda, and Y. Zhao, Carbon, Graphitization of diamond of different sizes at high pressure-high temperature. Carbon, in press (2004).

8. Qian J., T. W. Zerda, D. He, L. Daemen, Y. Zhao, Micron diamond composites with nanocrystalline silicon carbide bonding. Journal of Material Research, Vol. 18, No. 5, 1173-1178, (2003).

9. Qian J., G. Voronin, T. W. Zerda, D. He, Y. Zhao, High pressure high temperature sintering of diamond-SiC composites by ball milled diamond-Si mixtures. Journal of Material Research, Vol. 17, No. 8, 2153-2160, (2002).

10. Voronin G.A., T. W. Zerda, J. Qian, Y. Zhao, D. He and S. N. Dub, Diamond-SiC nanocomposites sintered from a mixture of diamond and silicon nanopowders. Diamond and Related Materials, Vol. 12, No. 9, 1477-1481, (2003).

11. Voronin G.A., C. Pantea, T. W. Zerda, L. Wang, Y. Zhao, In situ x-ray diffraction study of silicon at pressures up to 15.5 GPa and temperatures up to 1073 K. Phys. Rev. B, vol. 68, no. 2, pp. 020102, (2003).

12. Voronin G.A., C. Pantea, T. W. Zerda, J. Zhang, L. Wang, Y. Zhao, In situ x-ray diffraction study of germanium at pressures up to 11 GPa and temperatures up to 950 K. J. Phys. Chem. Solids, vol. 64, no. 11, pp. 2113, (2003).

13. Wang Z., Yusheng Zhao, D. Schiferl, J. Qian, Robert T. Downs, Ho-Kwang Mao and T. Sekine, Threshold Pressure for Disappearance of Size-Induced Effect in Spinel-Structure Ge3N4 Nanocrystals. Journal of Physics Chemistry B, Vol. 107, No. 51, 14151-14153, (2003).

14. Wang Z., Y. Zhao, D. Schiferl and H. S. C. ONeill, 2003, High-pressure Raman Spectroscopy of ferrite spinel ZnFe2O4. Journal of Physics and Chemistry of Solid, 64, 2517-2523, (2003).

15. Wang Z., Y. Zhao, D. Schiferl, C. S. Zha, R. R. Downs, and T. Sekine, Critical pressure for weakening of the size-induced elastic stiffness in spinel-structure Si3N4 nanocrystals. Applied Physical Letters, 83, 3174-3176, (2003).

16. Wang Z., R. T. Downs, V. Pischedda, R. Shetty, S. K. Saxena, C. S. Zha, Y. S. Zhao, D. Schiferl, and A. Waskowska, High Pressure x-ray Diffraction and Raman Spectroscopic Studies of the tetragonal Spinel CoFe2O4. Physical Review B, 68, 094101, (2003).

Many publications plus two patent applications (one allowed!)

Future R&D Directions

- **Improve matrix electric conductivity**

  (metal-ceramics bonding for EDM'able products)

- **Reduction of *P-T* synthesis conditions**

  (systematics of catalysts / solvents / additives)

- **Nanotube reinforcement to enhance toughness**

  (phys./chem. anchoring & "hairy" tube application)

Potential Machinery Applications

Novel B_6O-TiB_2 Nanocomposites

Much higher thermal stability T_c=1600K

Compared with diamond (900K) and cBN (1100K)

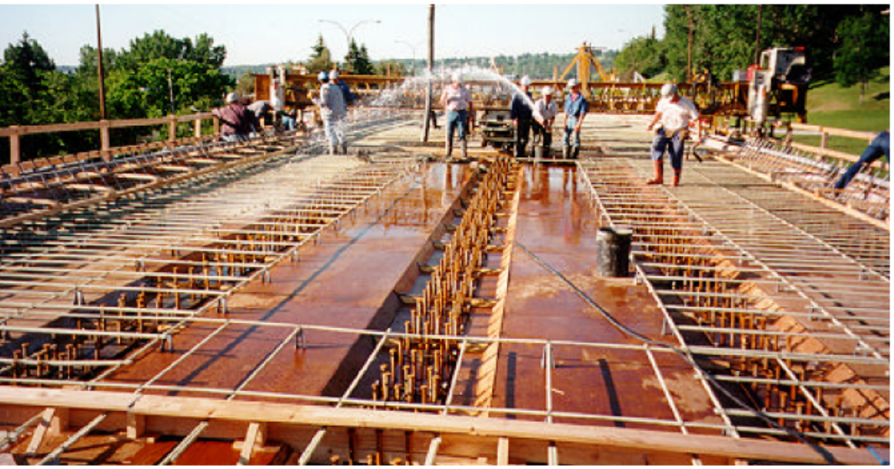
It is the hardest materials at T>700K

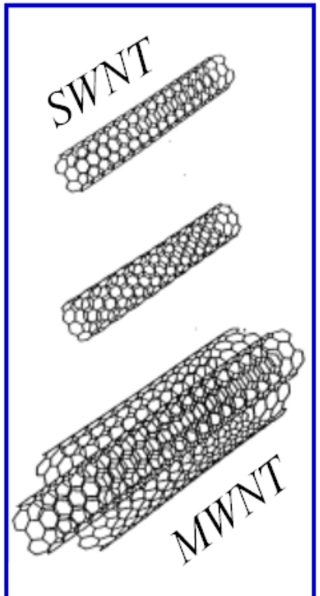
We expect to achieve great mechanical performances for Nanotube / Nanofiber Reinforced Composites.

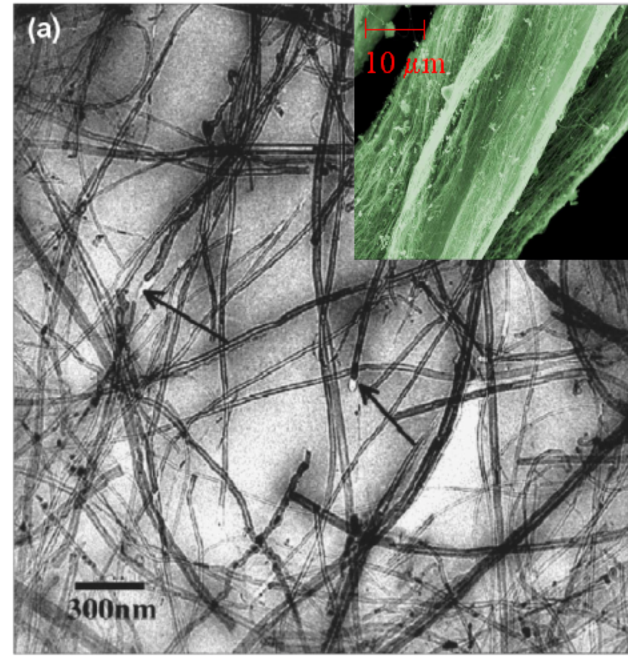
Especially, the enhancement of fracture toughness.

Steel Reinforced Concrete

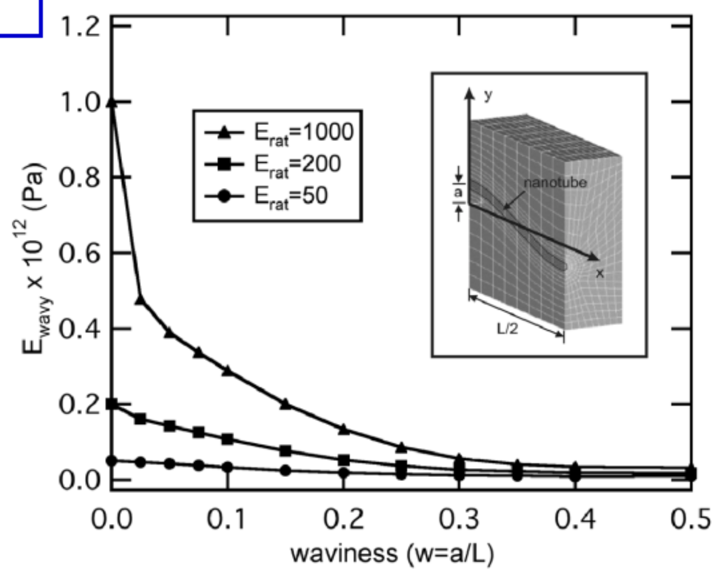
is essential to the construction industry







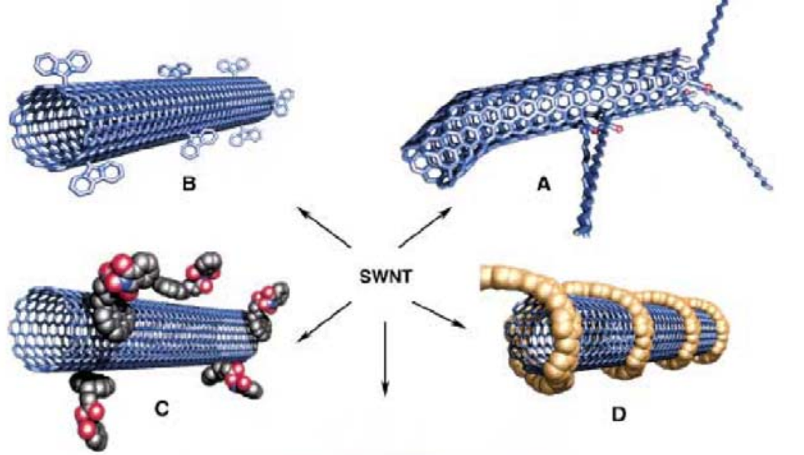
Nano-Synthesis

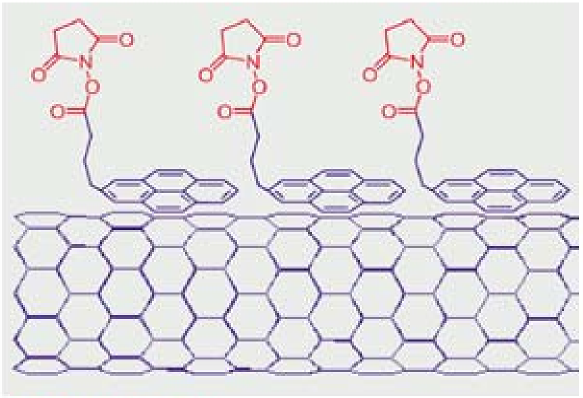


Nanotube: *extraordinary high tensile strength, high elastic modulus, and high strength-to-weight ratio* **!!!**

Material	Elastic Modulus	Maximum Strain	Yield Strength	Density	Strength-to-Weight Ratio
SWNT	648–1503 GPa	4%	34.5 GPa	1.4 g/cm^3	245
MWNT	400 GPa	1.5%	2.7 GPa	1.8 g/cm^3	14.5
Titanium	103 GPa	15%	0.9 GPa	4.5 g/cm^3	1.9
Aluminum	69 GPa	16%	0.5 GPa	2.7 g/cm^3	1.7
Steel	207 GPa	9%	0.8 GPa	7.8 g/cm^3	1.0 *(Normalized)*

The key to the successes of the nanotube-reinforcement is to enhance its "wet-ability" and "solubility" so that nanotubes can be incorporated with the matrix of composites





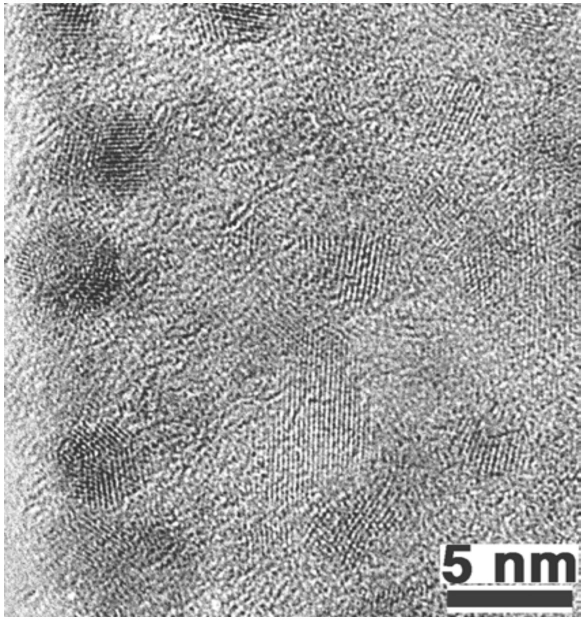
ANCHORED The pyrene group of a succinimidyl ester adheres to the nanotube wall, allowing proteins or other molecules to be attached at the ester function.

Synthesis of "hairy" nanotubes

Our Unique Approaches

*Homogeneous dispersion of the nanotubes in ceramic/alloy **amorphous** matrix*

*Physical anchoring and/or chemical anchoring onto functionalized "**hairy**" nanotube*



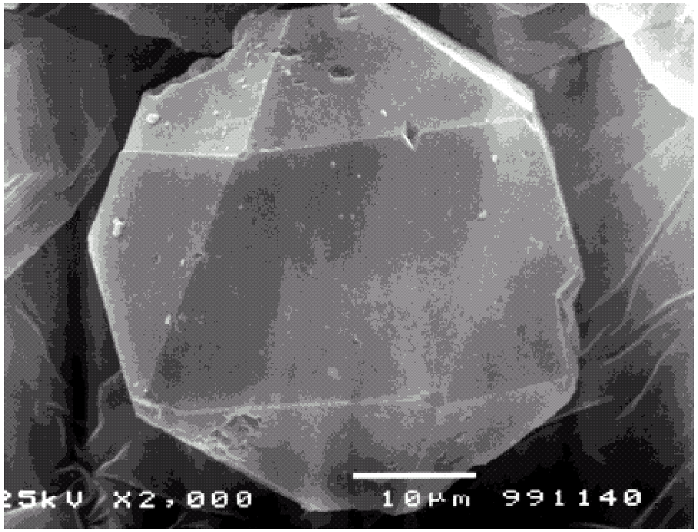
Amorphous matrix has intrinsically low contact-angle, readily to wet.

Amorphous matrix can greatly improves mechanical performance of nanostructured bulks

(1) to relax mismatches from adjacent unit cells corresponding to different phases;

(2) to absorb vacancies, dislocations, and impurities at the grain boundaries;

(3) to diminish surface energy and reduce residual stresses in nanocrystalline grains.



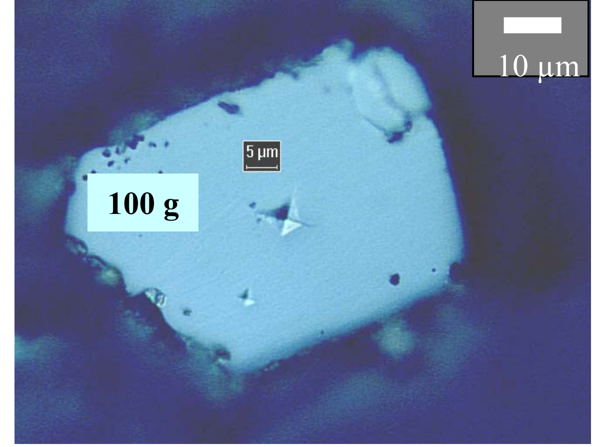
$16B + B_2O_3 \rightarrow 3B_6O$

5.5 GPa, 2200 K, 240 min

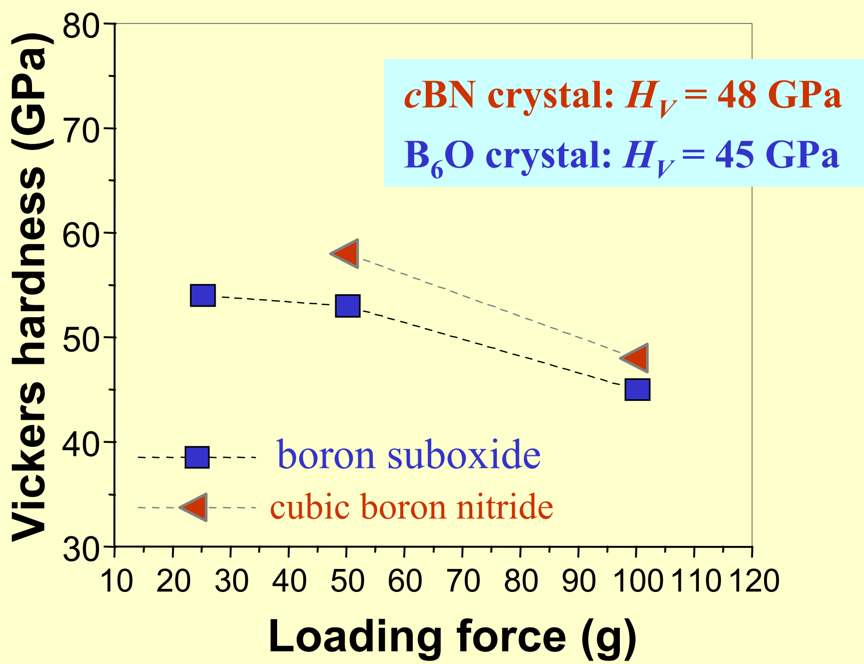
Icosahedra, multi-twinned

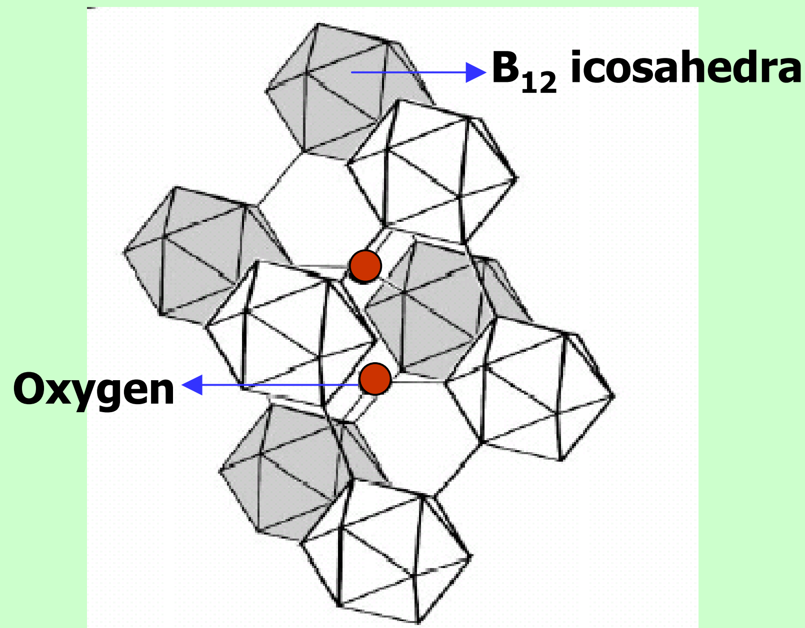
Published on *APL*

Highlighted by ***Nature***

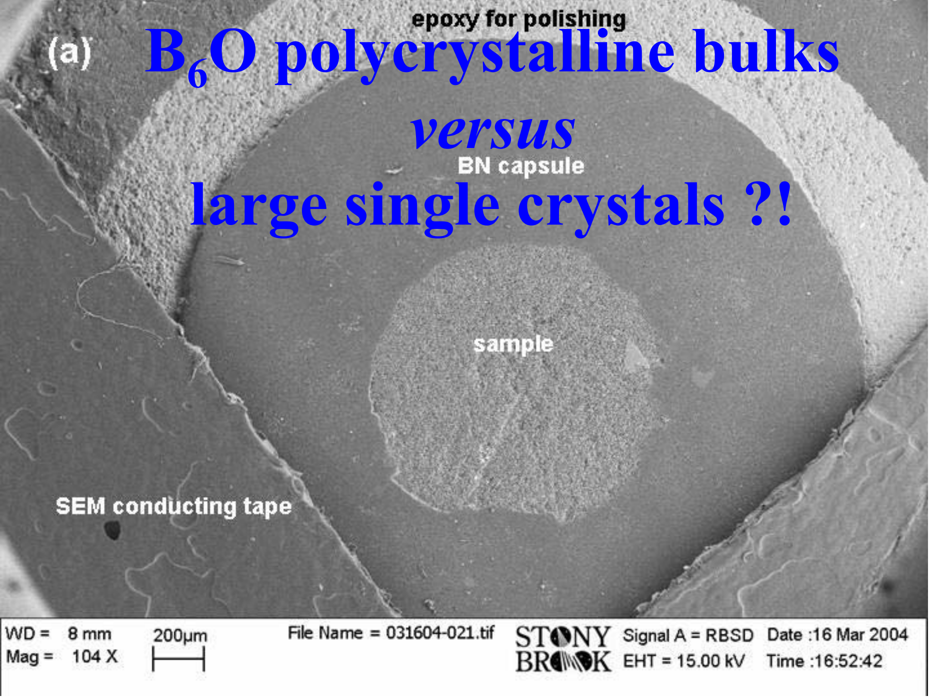


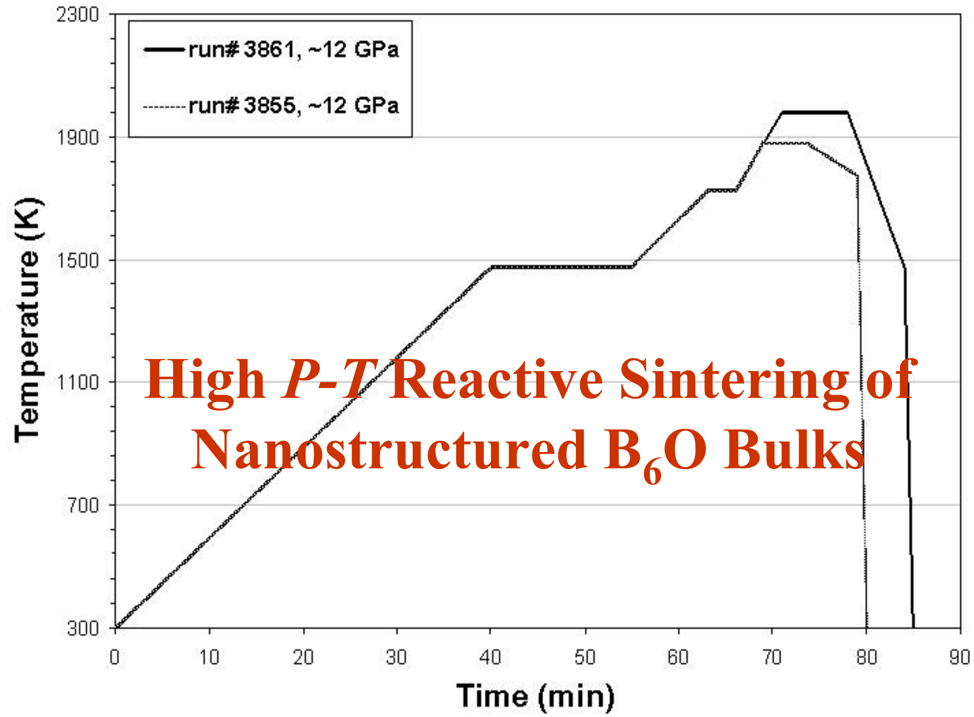
Super hardness, low density, high thermal stability, excellent chemical inertness & wear resistance

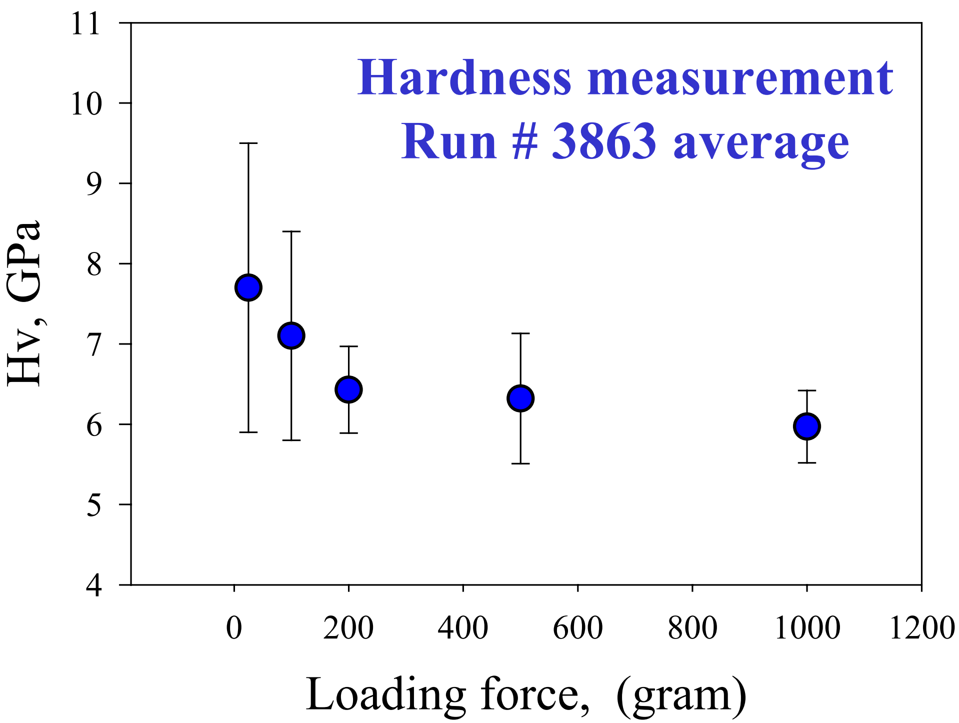


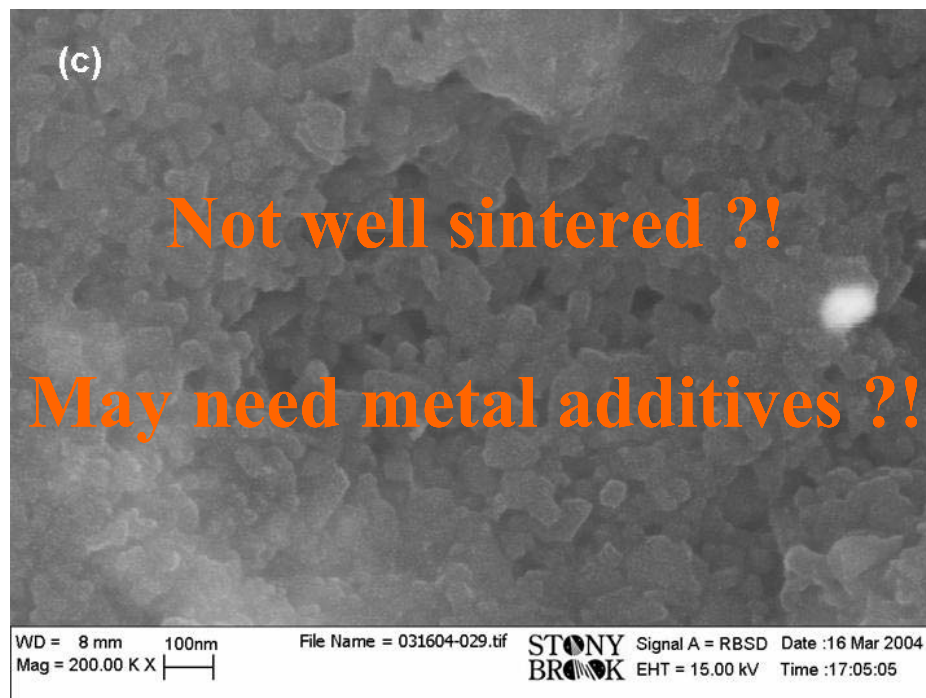


The structure of B_6O is built of eight icosahedra at the apexes of the rhombohedral unit cell. Each icosahedra is composed of twelve boron atoms. Oxygen atom are three-coordinated to boron atoms in separate icosahedra in the (001) plane.

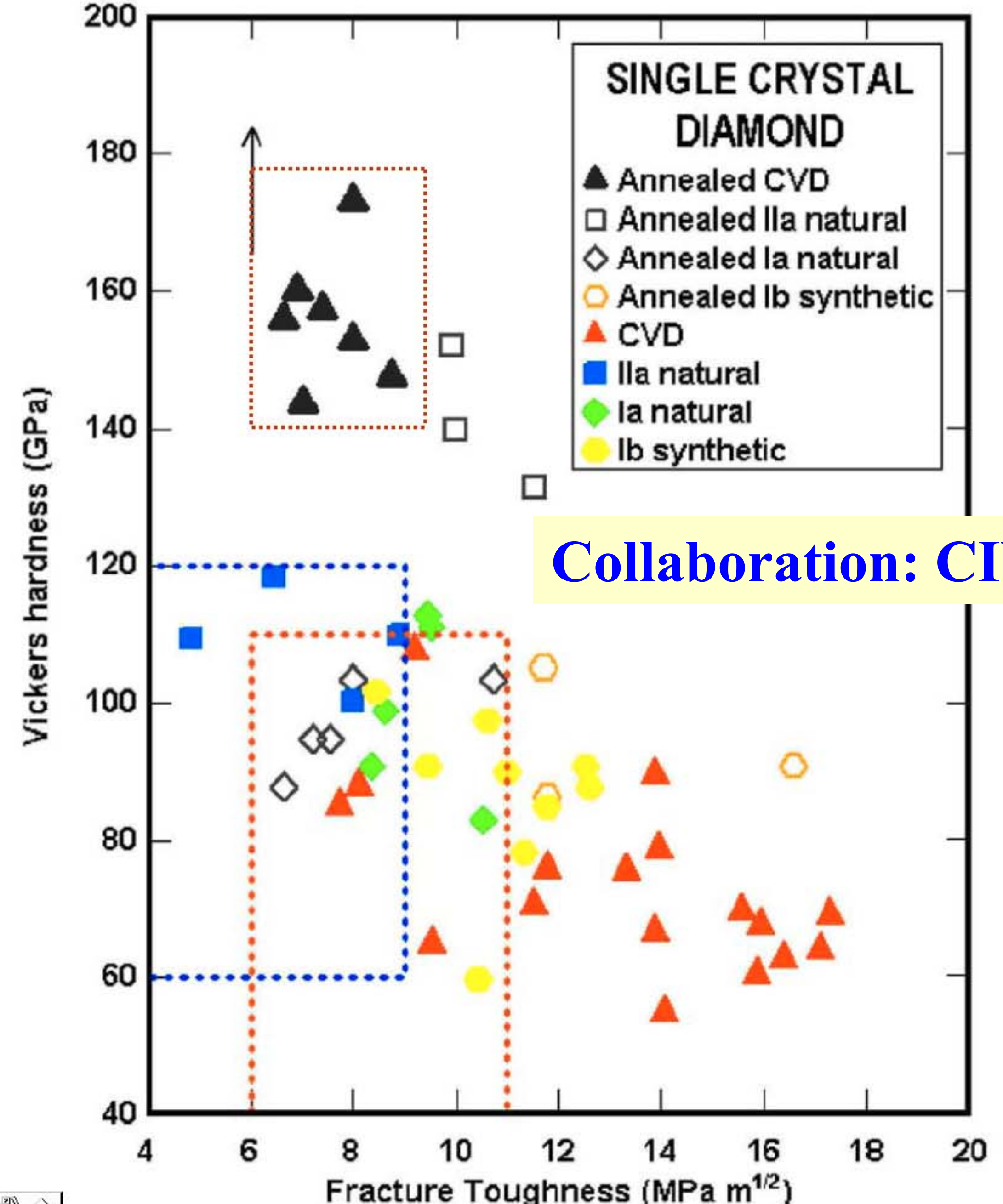

(a)
B6O polycrystalline bulks
versus
large single crystals ?!
epoxy for polishing
BN capsule
sample
SEM conducting tape
WD = 8 mm
Mag = 104 X
200µm
File Name = 031604-021.tif
STONY BROOK
Signal A = RBSD
EHT = 15.00 kV
Date :16 Mar 2004
Time :16:52:42

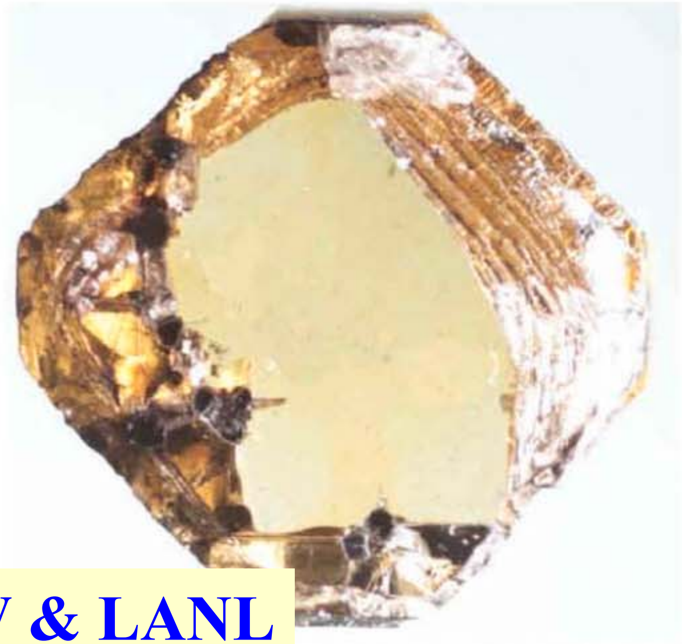

run# 3861, ~12 GPa
run# 3855, ~12 GPa
Temperature (K)
2300
1900
1500
1100
700
300
0
10
20
30
40
50
60
70
80
90
Time (min)
High P-T Reactive Sintering of
Nanostructured B6O Bulks


Hardness measurement
Run # 3863 average
Hv, GPa
11
10
9
8
7
6
5
4
0
200
400
600
800
1000
1200
Loading force, (gram)

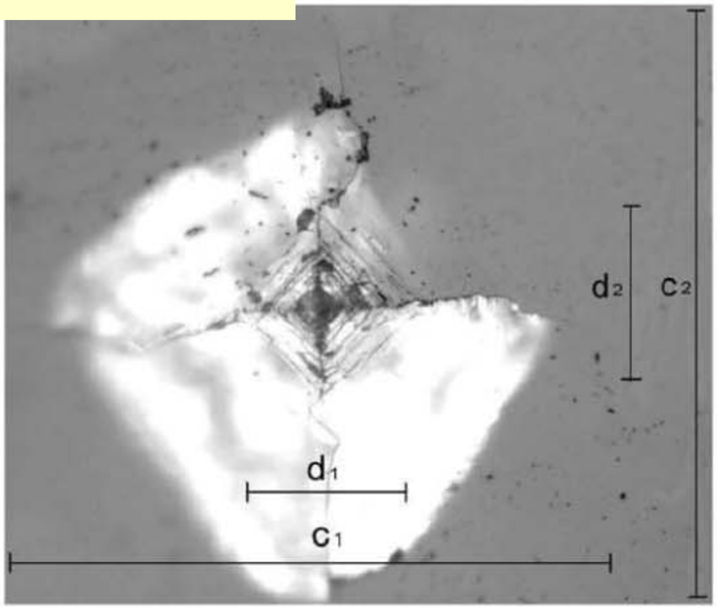

(c)
Not well sintered ?!
May need metal additives ?!
WD = 8 mm
Mag = 200.00 K X
100nm
File Name = 031604-029.tif
STONY BROOK
Signal A = RBSD
EHT = 15.00 kV
Date :16 Mar 2004
Time :17:05:05

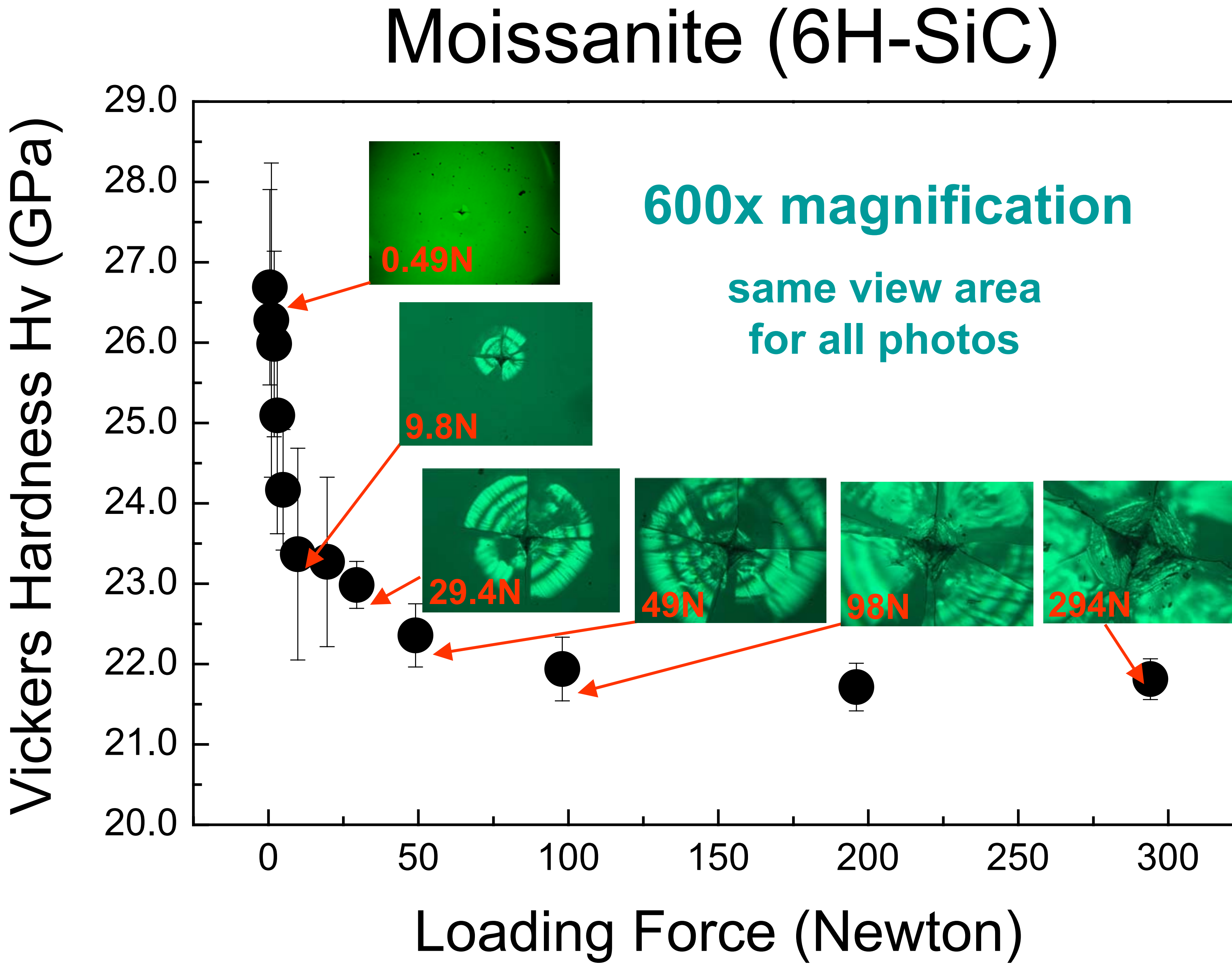
Ultra-hard Single Crystal Diamond from Chemical Vapor Deposition





Collaboration: CIW & LANL




Moissanite (6H-SiC)
600x magnification
same view area
for all photos
0.49N
9.8N
29.4N
49N
98N
294N
Vickers Hardness Hv (GPa)
29.0
28.0
27.0
26.0
25.0
24.0
23.0
22.0
21.0
20.0
0
50
100
150
200
250
300
Loading Force (Newton)